

REVIEW OF CERAMIC MEMBRANE REACTORS FOR THE WATER-GAS SHIFT REACTION IN COAL GASIFICATION COMBINED CYCLE CONCEPTS

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SUMMARY

The potential application of ceramic membranes for the water-gas shift reaction connected with high temperature hydrogen separation in coal gasification combined cycle concepts has been recognized. In the last few years research in ceramics, the availability of (porous) inorganic membranes and dense metallic membranes have improved the opportunity to develop perm-selective membranes. Such membranes can be used to enhance reaction conversions for some industrially important catalytic reactions as well as for high temperature gas separations. Particularly the above mentioned water-gas shift reaction deserves emphasis from the point of view of energy related applications.

In this report the possibilities for porous alumina, glass and carbon membranes have been discussed. Alumina and glass membranes can be used as a pure ceramic membrane or as a composite consisting of a ceramic support and a very thin layer of palladium or one of its alloys. Of these two options the most useful membranes for high temperature separation of hydrogen in the water-gas shift reaction process are alumina membranes or alumina/palladium composite membranes. Alumina membranes have good mechanical properties, very good resistivity to chemical attack and good thermal stability. However, the permselectivity of these materials is still limited.

Another very promising material is carbon. Membranes consisting of carbon combined with a cobaltoxide-molybdenumoxide catalyst can work as a catalytic membrane, which has the possibility of combining permselective and catalytic properties. In this latter case a very high tolerance to sulphur has been shown. By continuous separation of hydrogen in the reactor, thermodynamic (and kinetic) limitations are reduced and an improved hydrogen production is attained. Hydrogen to carbon dioxide separation factors up to 4.5 were obtained using the catalytic carbon membrane in the water-gas shift reaction process [1].

All information concerning the use of ceramic membranes and catalytic inorganic membranes in high temperature gas separation processes are reported based on laboratory scale investigations only. By combining the most promising catalyst and membrane materials for high temperature gas separation, it seems to be possible to shift the water-gas shift reaction far beyond its equilibrium, which leads to better economy of the reaction.

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1. INTRODUCTION

In the future coal will play an important role as one of the main sources of energy in the world. Because of the possibility of a climate change due to the emission of greenhouse gases the demand for clean coal technologies for energy generation, by increasing efficiencies and decreasing emissions, is growing.

Due to this awareness ECN has started the energy R&D programme ENGINE (Energy Generation In the Natural Environment). The Business Unit Fossil Fuels of ECN with the ENGINE sub-programme "H₂-CO₂ Technology" focusses on the use of coal for the production of energy by means of coal gasification in combination with the removal and storage of CO₂ [1]. Existing coal gasification technologies have to be improved to achieve these goals. Current commercial separation of CO₂ from synthesis gases takes place at lower temperatures, which drastically reduces efficiency of coal gasification plants. The efficiency of this process could be increased substantially if the gases can be separated at a higher downstream temperature. One of these improvements can be the use of ceramic membranes for high temperature separation of CO₂ and H₂ [2]. In case of H₂ removal the resulting CO₂ rich stream has to be purified in order to get a concentrated CO₂ product. The separated hydrogen can be burned in the combined cycle. Another possibility to reduce the cost of power generation is by combining the water-gas shift reaction with hydrogen separation using a catalytic membrane reactor. By continually separating hydrogen from the reactor, thermodynamic and kinetic limitations in the water-gas shift reaction can be changed leading to larger hydrogen yield due to equilibrium shift. The economics of the overall plant may further be made attractive by conducting the water-gas shift step as well as other down stream steps at high temperature and high pressure conditions [3].

To utilize this combined reaction and separation, hydrogen selective membranes capable of operating at 25-35 bar and 300-500°C are needed. In addition, the membranes should be tolerant to various contaminants in gasifier gas streams as, for instance, hydrogen sulphide. Under these conditions, currently existing, polymeric hydrogen selective membranes cannot be used [16]. Metallic palladium membranes are known to be hydrogen selective but they will rapidly degrade by the sulphur in the gas stream. Due to its low molecular weight, hydrogen may be separated selectively from

other gases by Knudsen diffusion, what means that gas species permeate independently of each other at a rate inversely proportional to the square root of their molecular weight. This mechanism, allowing hydrogen to permeate about 3.7 times faster than carbon monoxide and nitrogen, requires a membrane with pore sizes of the order of 20-100 Å. Inorganic mesoporous membranes such as ceramic and carbon with a permselective layer of the appropriate pore sizes are possible candidates for membrane reactors for water-gas shift reaction. Other possible membrane types are discussed elsewhere [2, 4]. The H₂-CO₂ separation has to be combined with the catalytic reaction by using a catalytically active and H₂ selective membrane or by using a packed catalyst bed and a membrane in one reactor.

The most important boundary conditions for these catalytic membranes in coal gasification concepts are summarized as follows [5]:

- temperature range : 300-500°C
- maximum pressure : 30-40 bar
- maximum pressure drop membrane : 30-40 bar
- resistant against : sulphur, H₂O, other trace elements.

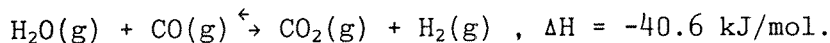
The goal of this report is to make a literature survey with respect to the technical and economic feasibility of inorganic membranes or membrane reactors with a permselective catalytic layer for simultaneous water-gas shift reaction and hydrogen separation. The reactors should process raw gasifier gas streams containing sulphur at 300-500°C and produce low-cost hydrogen for application in integrated gasification combined cycle power plants.

Remark: Microporous means materials having pores < 2 nm in diameter, mesoporous materials have pores between 2 and 150 nm (official IUPAC notation).

2. THE WATER-GAS SHIFT REACTION

2.1. General

The water-gas shift reaction is a reversible, exothermic chemical reaction, usually assisted by a catalyst. It is the reaction of steam with carbon monoxide to produce carbon dioxide and hydrogen gas:



The equilibrium constant K_p (equation 1) as a function of temperature is shown in Fig. 1 [6]. In the temperature range 315 to 480°C, expression (2) provides a good estimate of the equilibrium constant K_p .

$$K_p = \frac{[\text{CO}_2] \cdot [\text{H}_2]}{[\text{CO}] \cdot [\text{H}_2\text{O}]} \quad (1)$$

$$K_p = \exp [(4577.8/T) - 4.33] \quad (2)$$

where T is in K.

Equation 2 and Fig. 1 show that the equilibrium constant K_p decreases as temperature increases. For instance K_p is 11.8 at 400°C and 228 at 200°C. Hence, from the point of view of increased hydrogen production and reduced carbon monoxide content, it is desirable to conduct the reaction at low temperatures (Fig. 2). For instance, in the above example the CO-content at equilibrium can be 20 times lower at 200°C than at 400°C. Conversely, taking a 50% CO - 50% H₂ mixture to 1% CO with the shift reaction would require a steam-to-gas ratio of 3.5 at 370°C and a steam-to-gas ratio of 10.5 at 500°C. Dependence of CO-conversion as a function of the H₂O/CO ratio at four different reaction temperatures is shown in Fig. 3. Hence, from the point of view of steam economy and reactor volume, a lower reaction temperature is desirable. However, in order to achieve the necessary reaction rates, higher temperatures are often required. It can be seen that an ideal condition for the water-gas shift reaction would be the use of a catalyst active enough to operate at low temperatures where equilibrium is very favourable. Reaction pressure has a negligible effect

on the equilibrium of the shift reaction, since the number of moles of material in the shift reaction does not change during the course of the reaction.

In order to obtain maximum conversion of carbon monoxide the reaction is conventionally carried out in two stages. In the first stage an iron-chromium catalyst, operating temperatures in the range of 470-530°C and pressures up to 50 bar are used. In the second step a copper catalyst and operating temperatures in the range of 200-250°C are employed.

The water-gas shift reaction is of particular interest due to its industrial importance. The reaction is a step in many industrial processes, including hydrogen production. The demand for hydrogen, a product of the shift reaction, will become even greater in future years, since new uses for hydrogen are expected, such as use as a direct fuel.

2.2. Catalysts

2.2.1. General

A commercial application of the water-gas shift (WGS) reaction is raising the concentration of hydrogen in gas mixtures produced via steam reforming, partial oxidation of hydrocarbons or for ammonia synthesis. Copper-based catalysts are extremely active in this reaction, but these cannot be used at a high concentration of reactants because the activity would be deteriorated by sintering, due to the heat of reaction. The commercial process of the water-gas shift reaction usually consists of two convertors: the first being operated at high temperatures, between 350-400°C, with an iron-based catalyst having high thermal stability to suppress the concentration of CO, and the second being operated at comparatively low temperatures, ranging from 200 to 250°C, using a copper-based catalyst [7], Fig. 4.

Iron-based catalysts are so-called high-temperature shift catalysts, operating between about 320 to 450°C [8]. Iron oxide catalysts can tolerate a small quantity of sulphur and are fairly rugged overall [9].

Copper-based shift catalysts are so-called low-temperature shift catalysts, operating between about 200 to 250°C [10,11]. These catalysts have good activity at low temperatures and are therefore attractive since equilibrium is more favourable at lower temperatures. In addition to higher activity, another advantage claimed for the low-temperature shift catalysts is the higher selectivity and fewer side reactions at elevated pressures than high temperature shift catalysts.

Copper-based low-temperature shift catalysts are completely sulphur intolerant, since irreversible poisoning by even small quantities of sulphur compounds is occurring. Another material which is receiving increased attention as an industrial water-gas shift catalyst is sulphided cobalt oxide-molybdenum oxide on alumina [6]. This type of catalyst is insensitive to sulphur, and certain variations are claimed to possess good activity at both high and low temperatures. The results of the water-gas shift kinetic studies indicate that the catalytic activity of supported iron oxide is significantly lower than that of unsupported or bulk Fe_3O_4 . In addition iron oxide is two orders of magnitude less active on SiO_2 than on Al_2O_3 [12].

Two reaction mechanisms are playing important roles in the presence of a catalyst during the WGS reaction: a regenerative and an associative mechanism. They are described in detail in the Appendix.

2.2.2. Iron-based catalysts

High temperature shift catalysts in their active form consist of magnetite stabilized with trivalent chromium oxide. A typical example of the composition of a high temperature water-gas shift catalyst is as follows [6]: 74.2% Fe_2O_3 , 10.0% Cr_2O_3 and 0.2% MgO , balance volatiles. Operating temperatures are in the range of 330-530°C and operating pressures up to 50 bar are used [8, 13]. They are used effectively in the production of synthesis gas from gasification of coal. Operating lifetimes are typically 3-6 years. High-temperature shift catalysts alone may be used prior to carbon dioxide removal. However, in order to obtain maximum conversion of carbon monoxide the reaction is conventionally carried out in two stages, as shown in Fig. 4. Magnetite, the active component of high temperature shift catalysts, has long been known for its ability to promote the conversion of carbon monoxide to carbon dioxide at elevated temperatures. However, in the unstabilized form, it sinters rapidly under plant operating conditions and loses activity. The magnetite together with trivalent chromium oxide is incorporated in the iron oxide to assure the necessary thermal stability of the crystallite structure.

The high activity of the catalyst 15 (ICI Catalysts) [8] ensures that almost equilibrium concentrations are reached at the exit of the high temperature shift converter. This minimizes the load on the low temperature shift catalyst and maximizes production of hydrogen.

The most common cause of deterioration in the performance of a high temperature shift catalyst charge is due to the deposition of materials carried in the process gas stream. These usually originate from the refractories used in the reforming section or as trace impurities. They may be present in the process stream, at levels below the detection limits of standard analytical techniques. Also they can be due to a quench system. Deposition may occur in the gas cooler and boiler feed water pre-heater which follow the secondary reformer in most ammonia plants, and therewith affecting their heat exchange capabilities. This causes the high temperature shift catalyst to be operated at a higher temperature than desired resulting in a higher exit CO concentration, increased load on the low temperature shift converter and lower overall efficiency.

Deposition can also occur on the high temperature shift catalyst itself, in some instances to form a "crust" on the top of the catalyst. This increases the pressure drop in the bed as well as an apparent reduction of the catalyst activity by coating the active catalyst with an inert material. During operation the catalyst sinters, thereby resulting in a loss of surface area. Hoogschagen and Zwietening [14] studied the sintering phenomena quantitatively and found that the decrease in surface area could be correlated by the following equation:

$$\frac{1}{A^n} - \frac{1}{a_0^n} = Kt \exp(-E/RT) \quad (3)$$

where:

A_0 = initial surface area

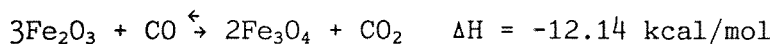
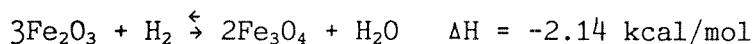
t = time

n = experimentally determined constant

K = equilibrium constant.

It was reported that a freshly prepared shift catalyst will have a surface area of 100 m²/g, but after 50-100 hr operation at 400°C, the surface area will be approximately 30-50 m²/g. Catalysts removed from commercial reactors after 2 months use may have a surface area of less than 15 m²/g. A common remedy for this problem, if the course of the deposition cannot be eliminated, is to remove the contaminated section of the bed and to replace it with fresh catalyst.

Two reactions are carried out when the high temperature shift activity is reduced in synthesis gas. In both cases haematite is reduced to the active species magnetite:



Residual sulphate in the catalyst from its production is reduced to hydrogen sulphide and removed in the gas stream. The small amounts of sulphur (< 50 ppm) have negligible effect on iron-based catalysts. At high sulphur levels the catalyst activity decreases approximately in proportion to the square root of the sulphur concentration. In practice the two steps occur at the same time. ICI's high temperature shift catalysts are used exclusively in hydrogen and ammonia plants. Table 1 shows data obtained from a coal gasification plant. The catalyst is divided into three beds, contained in a single reactor, with inter-bed cooling by addition of steam quenches.

Table 1. Operating data from a coal gasification unit.

	Bed 1		Bed 2		Bed 3	
Catalyst vol. m ³	7.7		15.4		15.4	
	Inlet	Exit	Inlet	Exit	Inlet	Exit
% dry basis CO	54	24	24	7	7	4
CO ₂	12	28	28	37	37	39
H ₂	32	45	45	53	53	55
Temperature °C	335	470	380	470	400	420
Steam to gas ratio	1.6	1.3	1.3	1.1	1.1	1.0
Wet space velocity h ⁻¹	19000		9900		10000	

2.2.3. Copper based catalysts

The gas stream leaving the high temperature shift reactor contains a substantial amount of unreacted CO (usually around 3%). In the second stage the gas stream is fed through a reactor containing a sensitive, highly active catalyst. The second reactor is operated at a somewhat lower temperature than the first (200-250°C). By carrying out the reaction in this way the temperature rise in the low-temperature shift reactor is in the region of 20°C. Consequently, the carbon monoxide content of the gas is considerably reduced, commonly to below 0.3% (see Fig. 3) [10,11].

The low temperature shift catalyst contains the active material, copper, in such a form that it has not only the required activity but it is also very stable. The small active copper crystallites are distributed homogeneously on a thermo stable support material. A low temperature shift catalyst is usually supplied as a mixture of oxides, while the copper oxide should be in a form that it can be reduced easily and quickly to the copper crystallites in the active form of the catalyst. In the reduced state the catalyst consists of copper supported on zinc oxide and alumina. If diffusion is not rate determining, the activity of the catalyst is directly proportional to the copper area and increases with increasing copper content.

Copper crystallites formed should not lose activity due to sintering during reaction in the temperature range 200-250°C. In addition, they should also be unaffected as far as possible, by traces of poisons in the process gas stream.

2.2.4. Sulphur resistant catalysts

The effectiveness of the catalyst is lowered by the relatively large sulphur concentrations found in coal gas. With iron catalysts, two steps for acid gas removal would be required: one to reduce sulphur levels before the catalyst and the second to remove acid gas after the catalyst. A highly active sulphur tolerant catalyst would be useful then since only one step would be required to remove acid gases.

A family of completely sulphur tolerant water-gas shift catalysts which has come under investigation typically consists of metals or mixed metals of Groups VI and VIII other than Fe and Cr, supported on alumina. The following catalysts have been studied for the shift reaction [6]:

- Mo-magnesia;
- Ni or Co with Mo;

- Ni or Mo or Co sulphides;
- Co/Mo/Ni with added alkali and
- Co-Mo with added alkali.

One particular catalyst which is claimed to be especially active is the combination of cesium carbonate, cesium acetate, potassium carbonate or potassium acetates together with cobalt and molybdenum. In its most active form, the catalyst is completely sulphided. This catalyst is not only sulphur tolerant but its activity is actually enhanced by sulphur.

The comparison of the activity of the most active Co/Mo/Cs catalyst to both iron based and copper-zinc based shift catalysts was taken from the literature. A reversible, first-order rate expression in CO was used to compare the activities. Rate constants for the catalysts are shown in Table 2 [6].

Table 2. Comparison of shift catalyst activities.

Catalyst	Pressure bar	Temperature °C	Pseudo first- order constant min ⁻¹
Fe-Cr	1	404	81.2
Zn-Cu-Cr	1	300	80
sulphided Co/Mo/Cs	1	404	6481
sulphided Co/Mo/Cs	1	300	418.9

It can be seen that the sulphided Co/Mo/Cs catalyst is much more active than either the Fe-Cr or Zn-Cu-Cr catalysts. Even though the comparisons may not be strictly valid in an absolute sense, they certainly point out that the sulphided Co/Mo/Cs catalyst is competitive in activity with the best industrial water-gas shift catalysts. The typical Co-Mo-Cs catalysts have the following composition:

MoO₃ - 12.5%

CoO - 3.5%

Al₂O₃ support

surface area - 270 m²/g

pore volume - 0.51 cm³/g.

The catalysts were impregnated with cesium acetate in varying amounts (from 0 to 1.048 g of CsOAc per cm³ of catalyst pore volume) and pretreated with 6% H₂S/94% H₂ at 550°C for 1½ hr.

The Arrhenius plot for the Co-Mo catalyst with no added cesium is shown in Fig. 5. The Arrhenius plots for the Cs-impregnated Co-Mo catalyst (0.3 g CsOAc per cm³) are shown in Figs. 6 and 7; with Fig. 6 being the low-temperature plot and Fig. 7 the high-temperature plot.

In conclusion, sulphided Co-Mo alkali metal catalysts appear to be exceptional water-gas shift catalysts due to high activity and sulphur tolerance. The use of these catalysts could increase significantly if large-scale coal conversion processes are adopted.

2.2.5. Summary

The advantage of the copper-based catalyst is the good activity and selectivity and the low temperature use (200-250°C) is favourable because of the equilibrium of the reaction. The main disadvantage of this catalyst is the absolute intolerance for sulphur (maximum allowed 0.1 ppm) requiring a thorough cleaning of the coal-gas.

The iron-chromium catalyst is used at higher temperatures (330-530°C) and has a lower conversion efficiency as the low temperature (copper based) catalyst. Due to this lower conversion two separate catalyst beds have to be used for high conversion. The catalyst can tolerate up to 50 ppm of sulphur.

The cobalt-molybdenum is a new type of catalyst for the water-gas shift reaction and it can be used successfully for this reaction due to the high activity and sulphur tolerance. The Co-Mo catalyst can be used in a relatively wide temperature range. There is no industrial experience with this type of catalyst.

3. MEMBRANE REACTORS

3.1. Introduction

Based on the materials used for the manufacture of membranes, they can be classified as organic or inorganic membranes [15]. Currently, a few organic polymeric membranes can withstand reaction temperatures up to about 180°C. In contrast to organic membranes, inorganic membranes are able to function at higher temperatures, for example commercially available mesoporous membranes made of silica glass or alumina can operate at temperatures as high as 800°C. The use of organic membranes in coal gasification applications is considered elsewhere [16].

Inorganic membranes can be divided into two main categories: dense and porous membranes. Commonly used materials for dense membrane preparation are palladium or palladium based alloys, platina, nickel, silver or even ceramic materials such as stabilized zirconia. Porous membranes are currently made from glass, alumina, zirconia or titania with pores which may vary from 40 Å to 10 µm. Gases can be transported through the membrane pores via bulk flow, molecular or Knudsen diffusion, surface diffusion, multilayer adsorption and capillary condensation or microporous activated diffusion [2]. Facilitated transport membranes will not be discussed here, see e.g. [2].

Dense metallic membranes have the advantage of very high selectivities since only certain species can be dissolved in their structural lattice. However, the permeabilities are at least a factor 100 lower than those of porous membranes.

In the following table a general overview of the mentioned gas separation mechanisms is given.

Table 3. Overview gas separation mechanisms for inorganic membranes.

Separation mechanism	Pore size (nm)	Separation factor	Permeability	Temp. range °C
Knudsen diffusion	2-20	low	high	< 600
Surface diffusion	2-5	low	high	< 200
Activated transport	0,5-1	high	modest	200-400
Molecular sieving	0,3-0,5	very high	low	< 500
Solution diffusion	-	high	very low	< 700

The selectivity or separation factor (α) of a membrane is defined as:

$$\alpha = \frac{y}{1-y} * \frac{1-x}{x} \quad (4)$$

with y = concentration fastest permeating component in the permeate

x = concentration fastest permeating component in the feed or retentate (see e.g. [2]).

Ceramic membranes were first produced in the early seventies, but until recently have not found any extensive industrial application. In recent years ceramic membranes have become commercially available with excellent pore size uniformity and good thermal and mechanical properties: resistant to pressures up to 30 bar [17,18]. Such membranes are finding broad applications in the food, pharmaceutical and electronic industries, for waste water treatment and in bioreactor applications [19]. High temperature ceramic membranes are also finding use in catalytic and reaction engineering applications [4,15,19,20].

Research on the suitability of ceramic membranes for gas separation was focussed on porous materials such as Vycor glass and alumina. Although these materials possess some permselectivity which is governed by Knudsen diffusion, the separation selectivity is very modest. This limits the applicability of these materials in its present form for high temperature application, especially in gas separation and membrane reactors where membranes must possess more selective diffusion properties.

On the other hand, there are few inorganic materials that have been known for selective permeation properties. For example, non-porous silica glass has a high selectivity for hydrogen. However, the productivity of these membrane reactors is severely limited by the poor permeability of the membranes.

Membranes that could be used in high temperature applications such as gas separation and membrane reactors, must possess the following characteristics:

- thermally stable;
- non-reactive, chemically resistant;
- good thermal properties, e.g. conductivity;
- permselective (high selectivity and high permeability).

The ceramic membranes can readily satisfy the first three requirements. However, the last requirement is a major limitation for the use of currently available inorganic membranes. To improve the permselectivity of the inorganic membranes and lose not too much of the permeability one must obtain a very thin membrane film with structural integrity, desirable thermal stability and high selectivity.

There are various techniques by which thin solid films may be prepared. These techniques can be e.g.:

- thermal evaporation (physical vapour deposition, PVD);
- cathodic sputtering;
- chemical vapour deposition (CVD);
- sol-gel techniques.

On laboratory scale some of these techniques are already employed successfully for the preparation of highly selective gas separation membranes.

Ceramic catalytic membranes have the inherent capability of combining reaction and separation in a single operation. This, in itself, is a significant advantage over having two completely separated unit operations of reaction and separation. The membrane provides for selective removal of one or more products and/or stable intermediates in parallel with the reaction. This drives the reaction continuously towards the product side and results in higher than equilibrium conversions, thus limiting the need for high temperatures (endothermic reactions) and pressures (not always favourable), and reducing recycle and down stream separation requirements. Furthermore, the use of membranes as both separators and reactors in a

single unit operation in catalytic reactions is capable of increasing the yield of the chemical processes [20].

The term "membrane reactor" has been used in the literature to describe a number of reactor configurations. The configurations of inorganic membranes and reactors can be done in various ways as is shown in fig. 8 [21].

The use of membranes in reaction processes can serve two different purposes:

1. To enhance the productivity of the chemical reactor, by continuously removing species from the reaction zone: shift the chemical equilibrium.
2. To influence the path of a chemical reaction, and residence time of the species and therewith affecting the reaction selectivity.

In one case the membrane can be a process unit separated from the reactor. It maintains only the separation function (passive membrane) and there is almost no interaction between reaction and separation. In fact, we have here two different processes connected in series.

In the second case the membrane itself is catalytic active.

This operation provides a strong interaction between reaction and separation, allowing the two processes to be integrated in one unit operation. The reaction is directly influenced by the membrane with continuous and selective removal of product from the reaction zone or with the controlled supply of reactant to the reaction zone. The membrane can either be inherently catalytic or catalytically modified with active species distributed in or at the entrance of the membrane pores as individual particles or as a layer. The catalytic activity is combined with the membrane properties: catalytically active membrane. In this way the strongest interaction between membrane transport properties and catalytic activity is achieved [21].

There are several methods for preparing catalysts: impregnation, precipitation, adsorption and dry mixing. The catalyst, in the case of a catalytic membrane, is incorporated in or onto the porous separator (membrane) and uses the membrane surface or pore surface as the catalyst carrier. The porous nature of the membrane makes impregnation and adsorption a preferred choice for preparation process.

Membrane reactors can be classified as follows [20]:

1. Type of reaction: homogeneous or catalytic.
2. Integration of membrane and catalyst functions:
 - a. Membrane separated from reactor: purification of reactant and/or product.
 - b. Membrane as part of reactor but not active:
 - catalyst packed on one side of the membrane;
 - catalyst deposited as a thin film on the membrane surface.
 - c. Membrane as part of catalyst/catalyst support:
 - catalyst deposited inside the membrane pores;
 - membrane material is catalytic.
3. Membrane configuration:
 - a. plate and frame;
 - b. spiral wound;
 - c. tubular or hollow fibre.
4. Component permeating or flowing through the membrane:
 - a. reactant permeating through the membrane as in membrane catalysis;
 - b. reactant flowing through the membrane for uniform distribution of reactant;
 - c. product permeating through the membrane to shift the section from equilibrium or reduce product inhibition.
5. Flow patterns on either side of the membrane:
 - a. co-current (flow on both sides of the membrane in the same direction);
 - b. counter - current flow.
6. Structure of the membrane:
 - a. large pores, not permselective;
 - b. micro- or mesoporous, permselective (molecular sieving, activated transport, capillary condensation with liquid flow, surface diffusion, Knudsen diffusion);
 - c. dense, permselective (solution and diffusion).

Membrane reactors offer several advantages, such as short contact time (not always an advantage), controlled pore size and distribution, high surface to volume ratio, less mass transfer resistance, and simultaneous reaction with separation.

3.2. Membrane reactors using porous ceramics

3.2.1. General

The earliest applications of membrane reactor technology utilized porous glass membranes. In 1979 Kameyama et al. utilized porous Vycor glass tubes to study the decomposition of H_2S to produce H_2 and S [31]. Conversions as high as twice the equilibrium limit were observed. Glass membranes have since then been utilized in other catalytic studies e.g. for the catalytic dehydrogenation of cyclohexane to benzene over supported Pt catalysts [22].

Most of the current literature on catalytic membrane reactor applications involves the use of Pd, Pd alloys with Ru, Ni and various metals from groups VI to VIII. The application of Pd membranes is based on the fact that Pd is highly permeable to H_2 but virtually impermeable to other gases and of course liquids. The development of Pd catalytic membranes has had a significant impact on proving and popularizing the concept of catalytic membrane reactors. The inherently low transmembrane fluxes, however, combined with the high cost of these membranes and the phenomena of metal sintering, embrittlement and fatigue have so far hindered the widespread industrial application of these membranes. It has been pointed out that a palladium membrane reactor gave low reaction efficiency compared with a microporous glass membrane reactor, because commercially obtainable palladium membranes exhibited low hydrogen flux at the operating temperatures in comparison with the flux through the microporous glass membranes [23]. In order to enhance the hydrogen flux by reducing the thickness of the palladium, it has been proposed to make a palladium-porous glass composite membrane, which was prepared by depositing a thin palladium film on the outer surface of a porous glass cylinder by a technique known as electroless plating [15, 24]. This composite membrane exhibited higher hydrogen flux than through a commercially obtainable palladium membrane, owing to the thinness of the palladium film [24,25].

Scientists from Oak Ridge National Laboratory are developing alumina membranes for separating hydrogen from coal gasification gases. However, inorganic membranes such as alumina that can withstand these temperatures, are currently only available with pore sizes between 30 and 40 Å, which for the present application is too large. For this reason alumina membranes having pore radii ranging from 7 to 13 Å have been developed. In prelimi-

nary tests, these membranes have held up to a variety of tests at varying pressures, and temperatures up to 260°C. Further research is expected to produce membranes with a mean pore radius below 5 Å [17, 32].

Different approaches to the phenomenon of H₂ permselective ceramic membranes were investigated by a team of scientists from California Institute of Technology in Pasadena, USA [26,27]. They have proposed a porous glass membrane with a H₂ permselective SiO₂ film. Films of amorphous SiO₂ were deposited within the walls of porous Vycor tubes by SiH₄ oxidation in an opposing reactants geometry. SiH₄ was passed inside the tube while O₂ was passed outside the tube. The two reactants diffused in mutually opposite direction to a narrow front inside the tube wall and forming a thin SiO₂ film. Once the pores were plugged the reactants could not reach each other anymore and the reaction stopped. Film deposition within the solid matrix prevents the formation of large pinholes and protects the deposited film from loss of adhesion or other mechanical damage. At 450°C and 0.1 and 0.33 bar of SiH₄ and O₂ respectively, the reaction was completed within 15 min. The thickness of the SiO₂ film was estimated to be about 0,1 µm. Measurements of H₂ and N₂ permeation rates showed that the SiO₂ film was highly selective to H₂ permeation. The H₂:N₂ flux ratio at 450°C varied between 2000 and 3000. Thermal annealing at 600°C has shown to reduce this selectivity. Thermal annealing in the presence of H₂O vapour decreased further the flux of H₂ and increased the flux of N₂. Permeation of H₂ is believed to occur through an activated diffusion mechanism. Applications of such H₂ permeable films to membrane reactors for equilibrium-limited reaction is proposed to improve H₂S decomposition.

A high temperature catalytic membrane reactor, containing a Pt-impregnated alumina membrane tube in a shell-and-tube configuration, was used to study dehydrogenation reactions by a team of scientists from the University of Southern California [19]. Experiments on the ethane dehydrogenation reaction to produce ethylene in this membrane reactor in the temperature range of 450-600°C show conversions up to six times higher than equilibrium conversions without removal of product hydrogen. This shift in equilibrium is due to the selective permeation of one of the reaction products i.e. hydrogen according to Knudsen diffusion. In the experiments they have utilized a trans-membrane pressure difference and an inert sweep gas on the low pressure side of membrane. The selectivity to ethylene, in an ethane steam cracker, is 78 to 82 mole percent employing a recycling step. Heterogenous catalytic processes developed using supported platinum on

alumina catalysts, have resulted in selectivities to ethylene of up to 98 percent. However, the very high temperatures necessary to obtain adequate yields have led to catalyst deactivation, due to metal sintering and coke formation. The ceramic alumina membrane tube (Membralox) used in this experiment was supplied by Alcoa. It consists of a multilayered composite porous alumina tube with an inner diameter of 7 mm and an outer diameter of 10 mm, and 250 mm in length. The first layer inside the tube is 5 μm thick and has a well defined pore structure with a pore diameter of 40 \AA . Successive layers are thicker, with progressively larger pores, supported on a thick support layer approximately 1.5 mm thick with a pore size in the range 10-15 μm . 95% of the resistance to flow and over 90% of the surface area lies in the first two top layers. The alumina membrane tube was wet impregnated with chloroplatinic acid solution up to 5 wt.%. It was dried overnight after which the tube was placed in the reactor and a 60% argon, 40% oxygen gas mixture was passed over the catalyst at 130°C. They found that the impregnation procedure did not noticeably lower the membrane permeability.

S. Uemiya et al. from Waseda University, Tokyo examined various porous materials with high thermal durability [28]. Among them, a porous alumina cylinder of Toshiba Cer. Co. Using this porous alumina cylinder as the supporting material, palladium-silver alloy films were prepared. A porous alumina cylinder (outer diameter 10 mm; wall thickness 1.3 mm) has a thin layer with a mean pore size of 200 nm which was supported on the outer surface of a matrix with a pore size of 10 μm . A thin film (5.8 μm) consisting of double layers of palladium and silver was formed on the outer surface of the cylinder by an electroless plating technique. Heat treatment of the coated cylinder was carried out at 900°C for 12 hr in a stream of argon. It was found that the silver melted to form an alloy with the palladium. Hydrogen selectivity was evaluated by separation of H_2 from an equimolar mixture of N_2 and H_2 , and hydrogen permeability was determined by use of pure grade hydrogen (99.99%) in the temperature range of 200-500°C, at a pressure difference of 1.94 bar, with the permeation side at atmospheric pressure. The rate of hydrogen separation through the supported miscible Pd-Ag alloy membrane having 23 wt.% of silver was compared with those through commercial membranes for hydrogen separation, porous Vycor glass and the other membranes of palladium and its silver alloys (fig. 9). The high hydrogen flux through the supported palladium-silver alloy membrane is related to the thinness of the film. This membrane exhibited

100% selectivity for hydrogen separation, even at comparatively low temperatures, around 200°C.

Applicability of the membrane at such a low temperature is attributed to inhibition of the coexistence of α - and β -phase palladium hydrides, which is mainly due to lowering of the spinodal decomposition temperature. The hydrogen permeability increased with silver content and reached a maximum at 23 wt.% of silver. The enhanced hydrogen permeability was related to the high hydrogen solubility. Disadvantage of this palladium-silver system is the brittleness of the palladium hydrides.

3.2.2. Application to the water-gas shift reaction

Complete conversion of the water-gas shift reaction is possible at high temperature of around 400°C in the case where the product, hydrogen, is separated from the reaction system by the use of a membrane [29]. The water-gas shift reaction was operated at 400°C by use of a double tubular type membrane reactor, the inner tube of which was a palladium membrane (thickness 20 μm) supported on a porous glass cylinder. The catalyst bed inside the membrane consists of a commercial $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ catalyst, Fig. 10 [29]. The membrane reactor provided higher levels of carbon monoxide conversion than could be expected on the basis of the equilibrium situation in a closed system. This should be due to a shift of thermodynamic equilibrium towards the product side, which was caused by selective and rapid removal of H_2 from the reaction system. Further, it was found that the amount of steam required to achieve reasonable levels of conversion could be reduced, and on the basis of a computer simulation, the high reaction efficiency attained by this membrane reactor is credited to the thinness of the palladium film. Fig. 11 shows a model of reaction and permeation in a palladium-glass membrane reactor. Fig. 12 shows the conversion of carbon monoxide as a function of palladium thickness. Fig. 13 and 14 show the effect of reaction pressure on the conversion of CO and as a function of the molar fraction of H_2 at 400°C [7,29].

G.R. Gavalas and C.E. Megiris have used in their experiment a porous glass membrane with H_2 permselective SiO_2 in a catalytic reactor for the water-gas shift reaction [30]. As a catalyst was used catalyst 29 such as iron oxide or iron chromium oxide. A mixture of carbon monoxide and water, as obtained from a coal gasifier, was utilized in this experiment. They have confirmed that the selective removal of hydrogen increases substantially the conversion of carbon monoxide. And so, starting with a 2:1 mixture of

H₂O and CO at 10 atm and 500°C, the equilibrium conversion of CO in a conventional reactor (no hydrogen removal) would be 73.4%. Employing the catalytic reactor system with a pressure of 10 atm inside tube and 1 atm in the outer space and a temperature of 500°C, would yield an equilibrium CO conversion of 92.7%.

3.3. Membrane reactors using porous carbon for water-gas shift reaction

A Research Triangle Institute project focusses on carbon composite microporous membranes [3]. Carbon was chosen for its chemical inertness and tolerance for water and sulphur gases, lower cost and better thermal expansion properties compared to ceramic membranes along with the ease of surface modifications. Carbon membranes can be prepared by pyrolysis of organic polymer membranes. The porosity and pore size of the carbons depend on pyrolysis conditions.

The commercially available carbon composite tubular membranes by Carbone USA Corp. are produced by the pyrolysis of an appropriate thermosetting polymer such as polyacrylonitrile. A carbon support tube is first prepared followed by addition of a permselective layer to produce desired (liquid) filtration characteristics. These commercially available carbon tubes have much larger pore sizes than desired for gas separation applications. These tubes provide the starting point to modify the membranes to make them more suitable for the catalytic membrane reactor application to maximize hydrogen production. The above mentioned project consists of three major components:

- modification of the commercially available carbon composite mesoporous tubular membranes to improve catalytic activity and to improve hydrogen separation properties;
- testing a modified membrane using simulated coal gas in high temperature high pressure environment to determine the improvement in hydrogen yield due to continuous hydrogen separation during water-gas shift reaction;
- economic and technical evaluation of this process on a commercial scale.

In order to make the commercial carbon tubular membranes suitable for gas separation and water-gas shift reaction, their pore size must be reduced and they have to be coated with a suitable water-gas shift catalyst. The deposit of a polymer precursor has been prepared only by dipping and in-situ polymerisation. Based on a literature review, cobalt/molybdenum oxide

catalysts were chosen as the catalysts to be used for the water-gas shift reaction.

The permselective layer thickness of the unmodified carbon membrane tubes was about 12 μm for the 0.2 μm pore size tubes and about 18 μm for the 1 μm pore size tubes.

The H_2/N_2 selectivity, defined as $K_{\text{hydrogen}}/K_{\text{nitrogen}}$, ranged from 2.2 to 2.6 which is lower than the Knudsen selectivity.

Although by coating the tubes, the permeabilities for individual gases were reduced by a factor of as much as 10 to 20, the hydrogen selectivities with respect to other gases did not improve significantly. The observed selectivities of modified membranes ranged from 2.4 to 2.7 and the hydrogen permeabilities ranged from 6×10^{-7} to 6×10^{-6} (scc/sec) \cdot cm/cm²/mm Hg ($\approx 1.3 \times 10^{-3}$ - 1.3×10^{-4} mol/m² \cdot s.Pa, calculation with layer thickness of 15 μm).

The low pressure/low temperature permeation data indicate contribution by both the Knudsen diffusion and viscous flow. But the high temperature high pressure reactor system can be operated at controlled transmembrane pressures where consequently minimum transmembrane pressure will suppress viscous flow through the membrane and promote diffusive separation between gases. This was observed during tests using an unmodified carbon membrane tube in the high temperature high pressure reactor system at 21.6 bar and 400°C. Simulated dry coal gas consisting of 36% H_2 , 45.6% CO, 17% CO_2 and 1.4% H_2S was passed through the membrane tube. Pure nitrogen was passed on the sweep side.

The permeation rates of gases through the membrane were determined from analysis of the exit gas streams. Hydrogen to carbon monoxide separation factors up to 3.5 and hydrogen to carbon dioxide separation factors up to 4.5 were obtained under such conditions. The Knudsen diffusion based membranes will provide a maximum selectivity of 3.7, between hydrogen and CO, the primary product and reactant for the water-gas shift reaction, respectively. This reaction is limited by thermodynamic equilibrium at high temperatures. At 425°C, the equilibrium constant is about 10. Thus, with a typical coal gas composition, mentioned earlier, and addition of stoichiometric amount of water the maximum conversion of CO would be limited to 63%. Selective separation of hydrogen will shift the equilibrium thus producing more hydrogen. However, due to high initial concentration of CO and only a moderate separation factor of 3.7 it may be advantageous to let the reaction proceed to near equilibrium conditions first, before beginning hydrogen separation. This would minimize the permeation of CO

to its lowered concentration in the gas phase, and allow its reaction before separation. Such an arrangement can easily be implemented in a carbon catalytic membrane reactor [3].

3.4. Discussion

As mentioned earlier, for high temperature gas separation and reaction, the membrane must possess good mechanical and thermal properties, good thermal stability and permselectivity as well as good chemical resistivity. Inorganic membranes made from alumina, glass and carbon satisfy the requirements of mechanical and thermal properties. Glass membranes have a lower mechanical strength than alumina membranes. Alumina and carbon membranes have very good chemical resistivity, however, glass membranes show sensitivity to working conditions. It was found that the H₂ permeability of glass membranes is lowered significantly during heating in a H₂O-containing atmosphere.

Inorganic membranes obtained from composites alumina or glass and palladium or palladium alloys have modest permeability and good selectivity, when governed by a very thin layer of palladium. But the Pd-membranes are very expensive and are characterized by the phenomenon of metal sintering and fatigue. On the other hand the ceramic membranes obtained from porous alumina till now have too low selectivity to gases. The size of the pores has a strong influence on the selectivity of alumina membranes. Pores with a diameter of about 5 Å are preferred. Alumina membranes with such pore radii are under investigation by scientists from Oak Ridge National Laboratory. A problem with these membranes can be the thermal stability of these small pores. Porous glass membranes with a perm-selective SiO₂ layer are characterized by a good perm-selectivity at the temperature range of 400-500°C, but their thermal properties and chemical resistivity is much lower than membranes made from alumina.

Attention deserve the carbon membranes which can meet almost all requirements; they are chemically inert, they have good tolerance for water and sulphur gases, they have better thermal expansion properties and are cheaper in comparison to ceramic membranes and the ease of surface modifications. But till now the selectivity of these membranes is too low. They can be used as catalytically active membranes what offers an inherent ability to combine reaction, concentration and product separation in a single operation.

The Co-Mo-oxide catalysts are recommended to use in such active membranes because they are fully resistant to sulphur.

All above discussed membranes were tested up to now on a laboratory scale only.

4. EVALUATION

As mentioned earlier the water-gas shift reaction is conventionally carried out in two stages in order to obtain maximum conversion of carbon monoxide. However, it is possible to carry out this reaction in one stage employing a sulphur tolerant catalyst at a temperature of 200-400°C. A family of completely sulphur resistant water-gas shift catalysts is currently under investigation. Mostly they are Co-Mo-based catalysts.

From the point of view of economy it is necessary to carry out the water-gas shift reaction at temperatures as low as possible just above 200°C where the equilibrium is very favourable. The temperature has to be above the dew point of water. Improvement in the field of the reaction can be achieved too by the use of catalytic membranes which have the possibility of combining the permselective and catalytic properties. By continuous separation of hydrogen from the reactor, thermodynamic and kinetic limitations are reduced and an optimum hydrogen production is attained. For such purpose a suitable membrane should be chosen.

As mentioned in chapter 3.1 the membrane must possess good mechanical and thermal stability, permselectivity as well as good chemical resistivity. Inorganic membranes made from alumina, glass or carbon satisfy the requirements of mechanical and thermal properties. Glass membranes have a lower mechanical strength than alumina membranes. Alumina and carbon membranes have very good chemical resistivity. Glass membranes coated with SiO₂ show sensitivity to working conditions. It was found that the H₂ permeability of these membranes is lowered significantly during heating in H₂O atmosphere. SiO₂ coated porous glass membranes are characterized by a good permselectivity at a temperature range of 400-500°C, but their thermal properties and chemical resistivity are much lower than membranes made of alumina.

The majority of scientists used porous glass membranes in their experiments because they are commercially available and are very useful in scientific experiments. Inorganic membranes obtained from composites alumina or glass and palladium or palladium alloys have modest permeability but good selectivity, when governed by a very thin layer of palladium. But the Pd-membranes are very expensive and are characterized by the phenomenon of metal sintering and fatigue. On the other hand the ceramic membranes obtained from porous alumina till now have too low selectivity to gases.

The size of the pores has a strong influence on the gas selectivity of alumina membranes. Pores with a diameter of about 5 Å are preferred. Alumina membranes with such pore radii are under investigation by scientists from Oak Ridge National Laboratory.

Attention deserve the carbon membranes which can meet almost all requirements; they are chemically inert, they have good tolerance for water and sulphur gases, they have better thermal expansion properties and are cheaper in comparison to ceramic membranes. Furthermore, the ease of surface modifications is an advantage. But till now the selectivity of these membranes is too low. They can be used as catalytically active membranes what offers an inherent ability to combine reaction, concentration and product separation in a single operation.

The Co-Mo-oxide catalysts are recommended to use in such active membranes because they are fully resistant to sulphur attack. Unfortunately all above discussed membranes were tested up to now on the laboratory scale only. However, the future utilization in industry scale only alumina and carbon membranes can be envisioned.

It is expected that both can work in water-gas shift reactors for quite a long time, approximately a few years, thanks to their good chemical resistivity, good mechanical strength and good thermal stability up to 500°C. Till now their weak point is low selectivity which is connected with too high a magnitude of pores. However, it can be expected that this problem will be solved in the near future.

The question which is still open is: should the water-gas shift reaction be carried out using a reactor with a separate sulphur resistant catalyst bed and a separate membrane or in one reactor with a catalytic membrane. From economic point of view the second solution is probably more favourable but on the other hand it creates a bigger challenge and more problems for scientists and engineers. Furthermore, it can be questioned whether the small amounts of catalyst involved in the active membrane concept are sufficient to give the required overall activity.

5. GENERAL CONCLUSIONS AND RECOMMENDATIONS

1. On a lab scale it has been shown that both passive and active catalytic membrane reactors can increase the conversion of chemical reactions by a combination of a catalytic step and selective removal of one of the products.
2. Specific to the water-gas shift reaction it was found that, depending on the hydrogen partial pressure in the unpermeated gas stream, almost 100% conversion is possible at 400°C at a steam to carbon monoxide ratio of 1 with a Pd coated porous glass membrane. By using a membrane reactor, an improvement in the reaction economy therefore seems possible not only because of the higher conversion and lower use of steam compared to the normal catalytic conversion but also because of the combination of two stages of the coal gas treatment into one stage.
3. More research on catalysts with high activity for the water-gas shift reaction and resistivity against sulphur is necessary.
The cobalt-molybdenum catalyst seems to be promising.
4. Also better membranes, with high permeability and a high selectivity to hydrogen have to be developed.
5. Research on the combination of different types of membrane materials and catalysts should yield a good combination for a catalytic membrane reactor with high conversion of the water-gas shift reaction. For example the promising Co-Mo catalyst should be combined with microporous (activated transport) membranes. These membranes should be stable.
6. Considering the knowledge collected up to now and the experience in the area of gas separation we suggest that the highly selective alumina membranes preferably in combination with sulphur tolerant Co-Mo-based catalysts should be developed at ECN.

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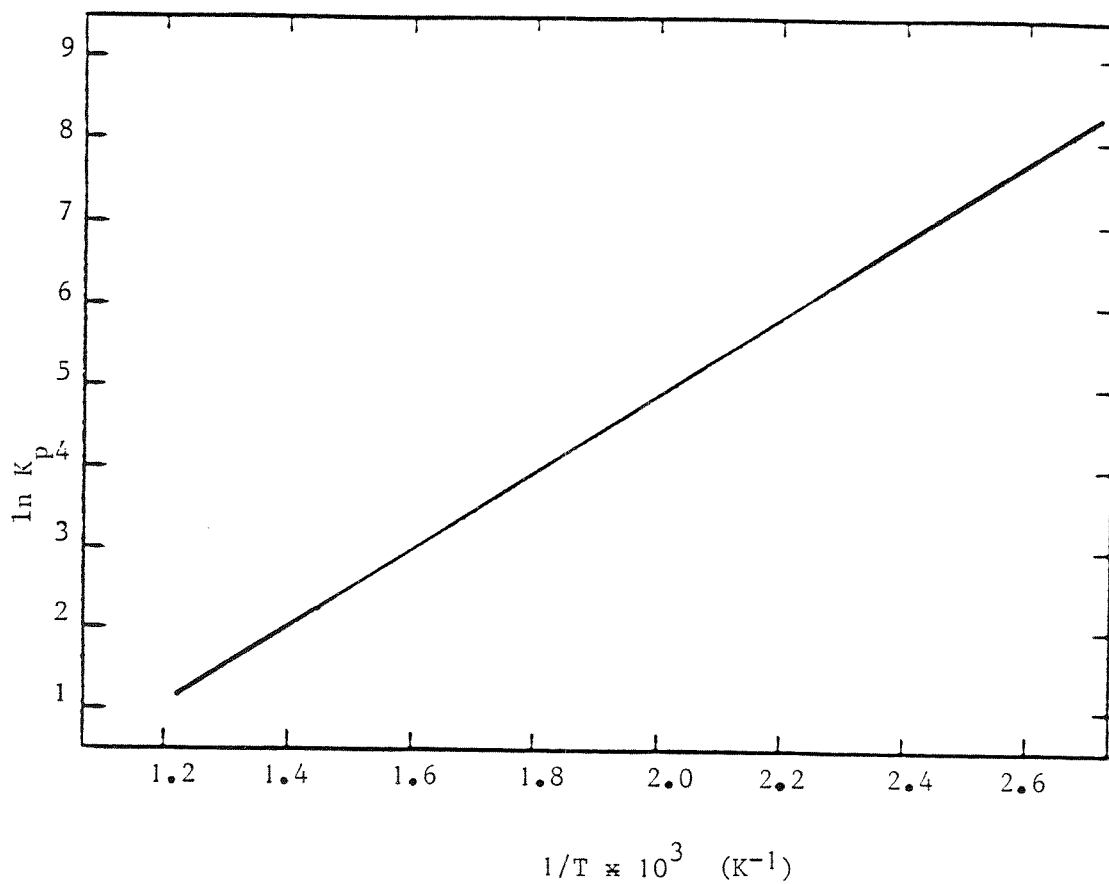


Fig. 1. Equilibrium constant as a function of temperature.

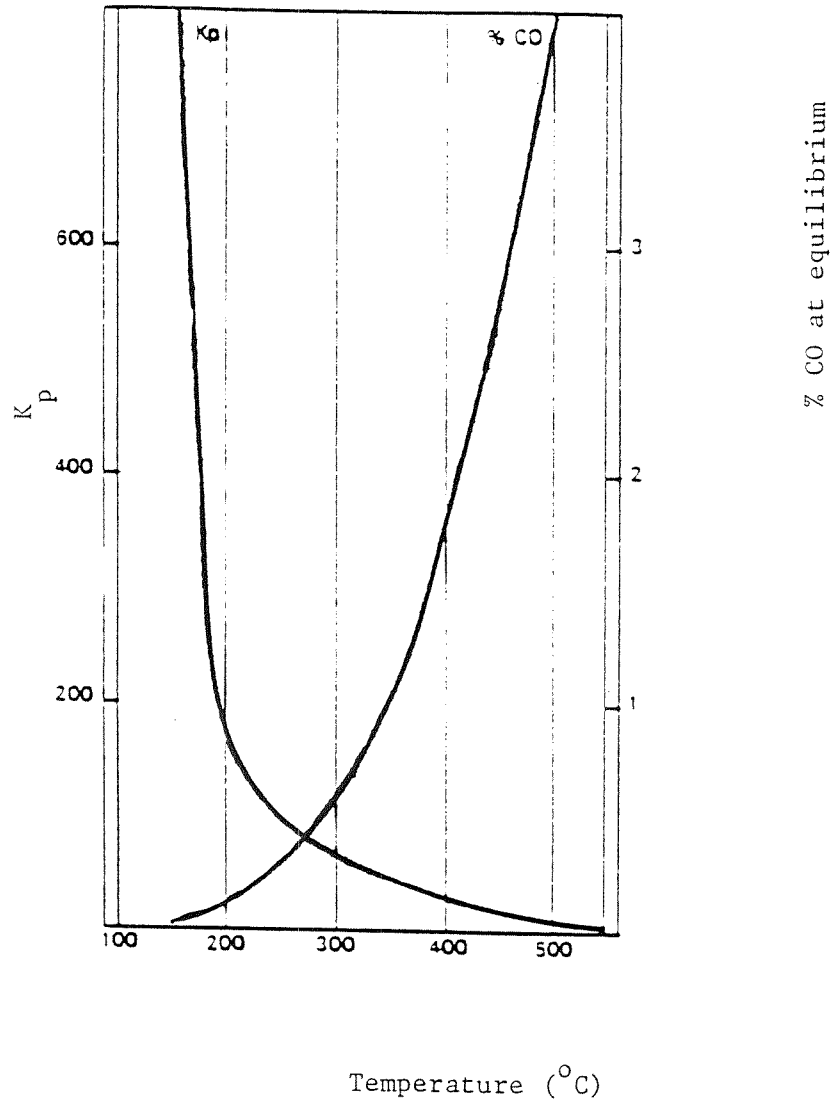


Fig. 2. Temperature dependence of K_p for the water-gas shift reaction, and equilibrium percentage of carbon monoxide in a particular gas mixture.

CO-shift (isothermal).
Clean fuel gas (Shell).

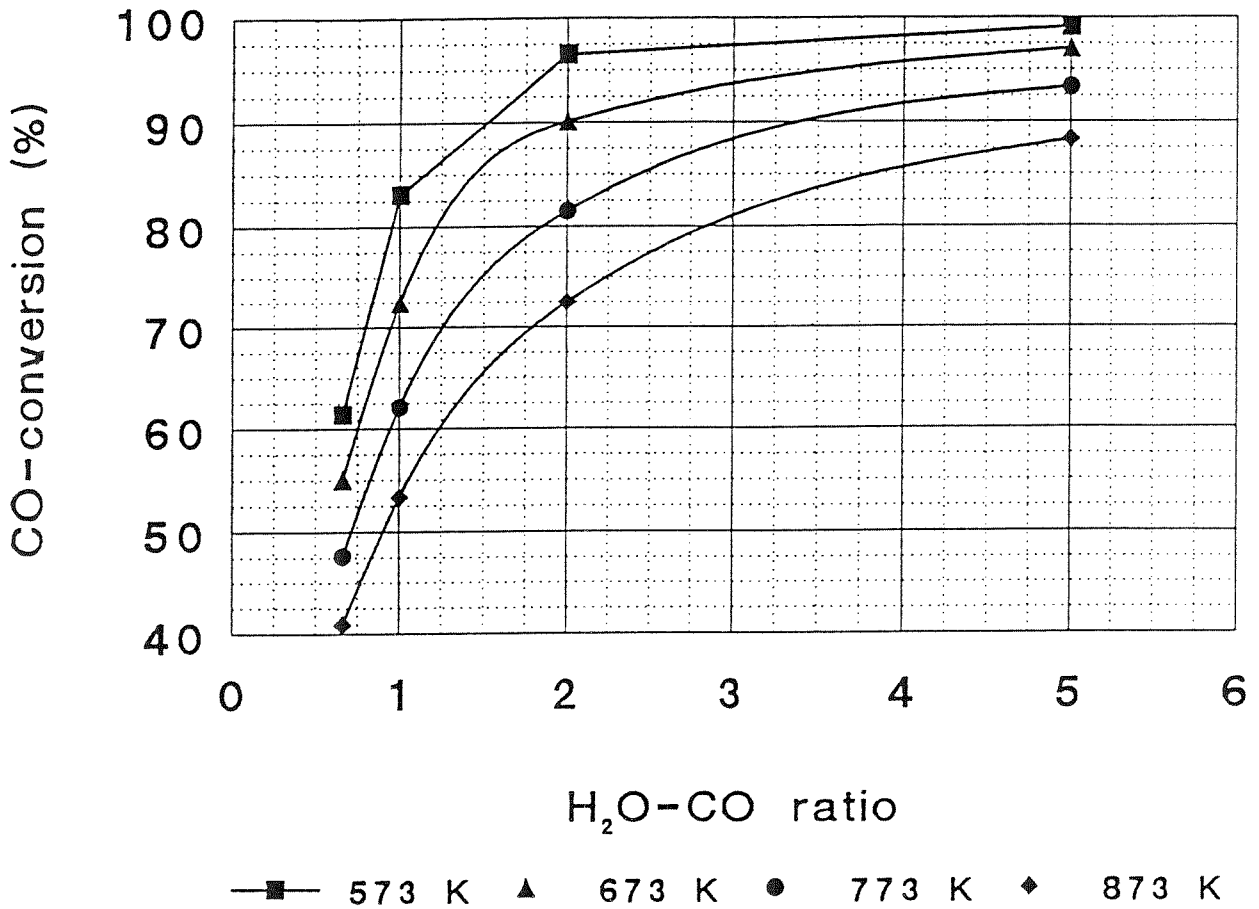


Fig. 3. CO-conversion of the shift reaction as a function of H₂O/CO ratio at four temperatures.

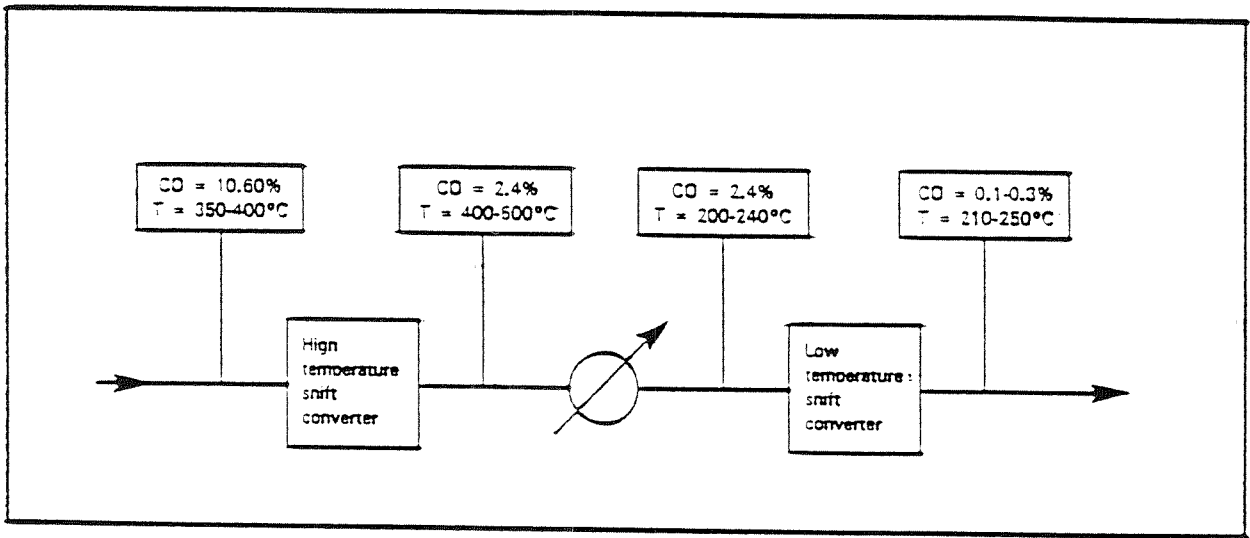


Fig. 4. Typical CO conversion in two stages.

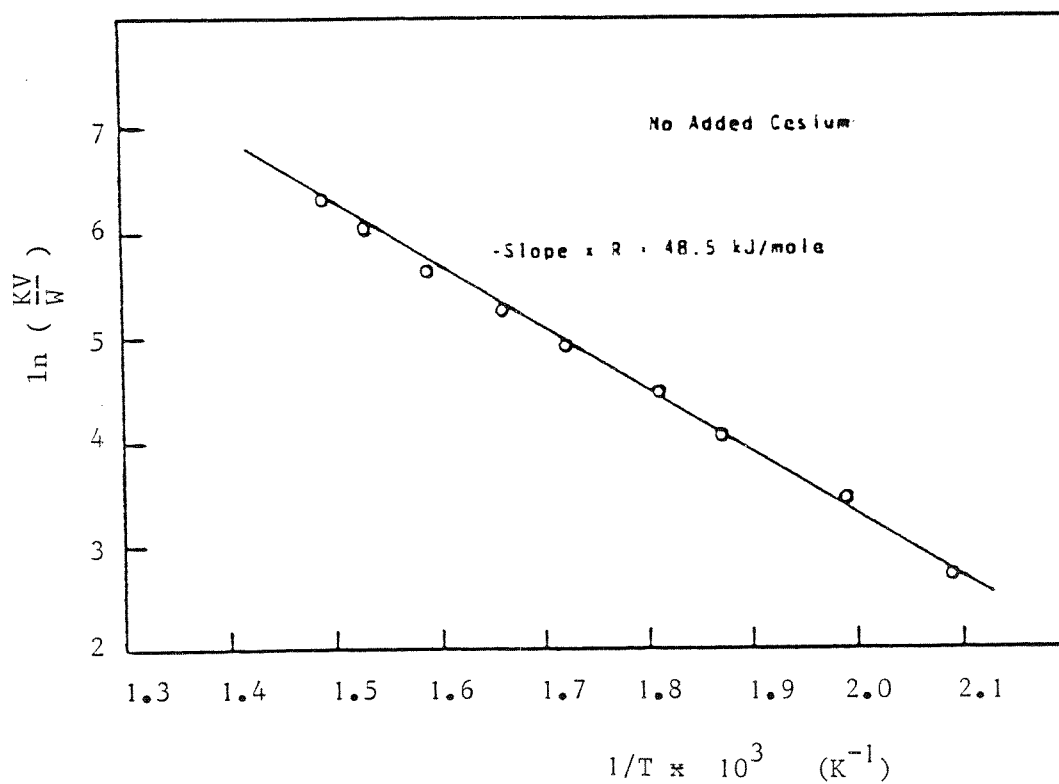


Fig. 5. Arrhenius plot for unimpregnated catalyst.

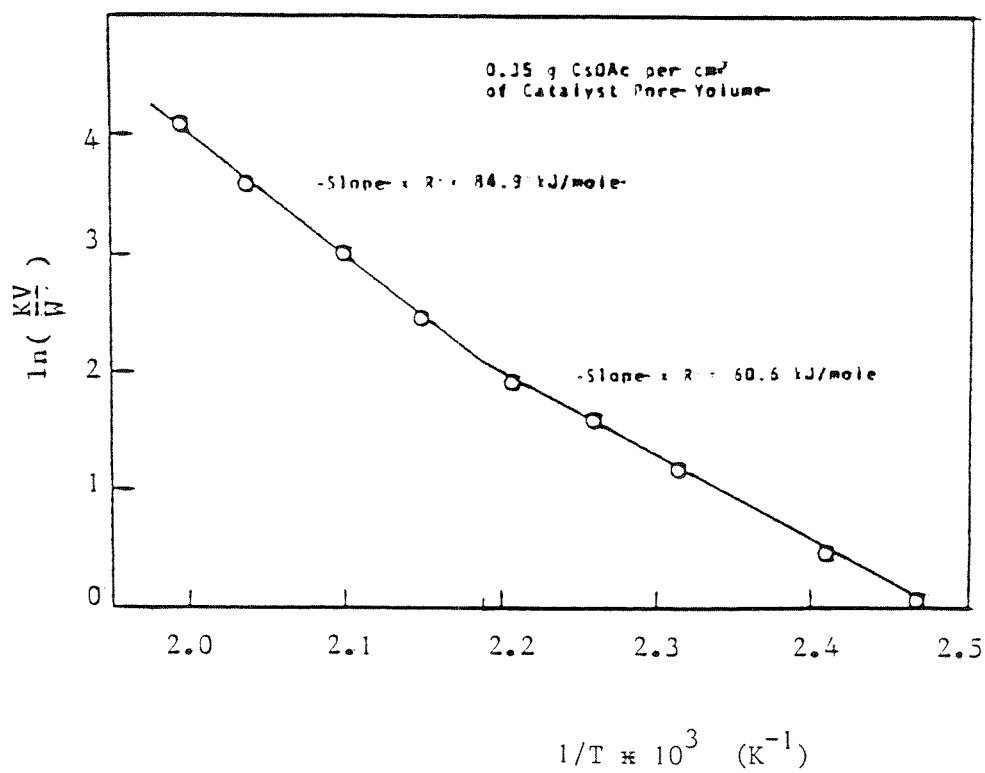


Fig. 6. Arrhenius plot for cesium-impregnated catalyst between 132 and 228°C.

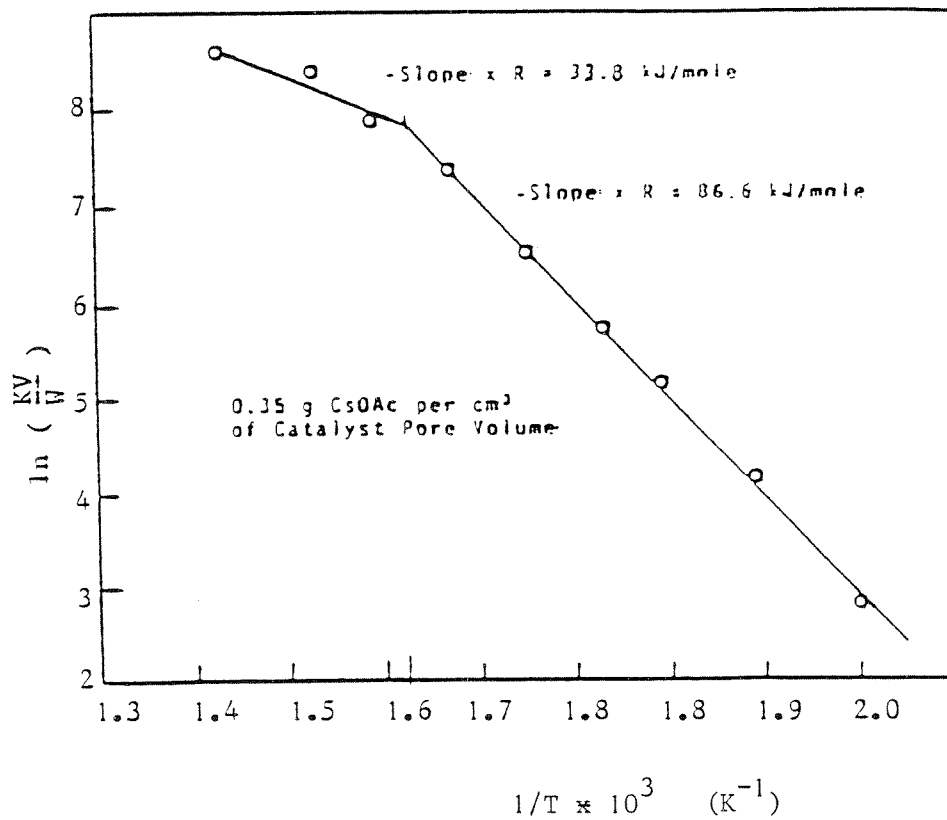


Fig. 7. Arrhenius plot for cesium-impregnated catalyst between 202 and 402°C.

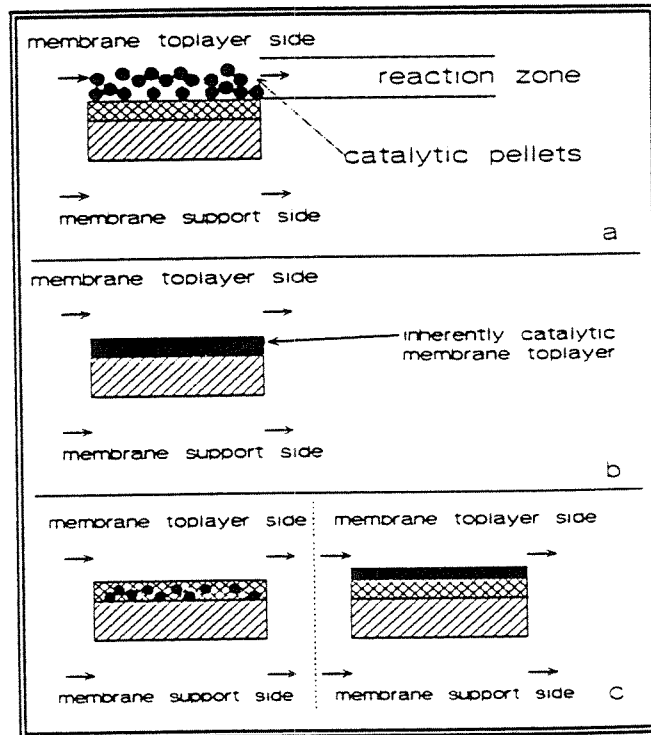


Fig. 8. Different membrane/catalyst combinations (a) the catalyst is packed next to the membrane; (b) the membrane is inherently catalytic; (c) the membrane is modified with catalytically active components.

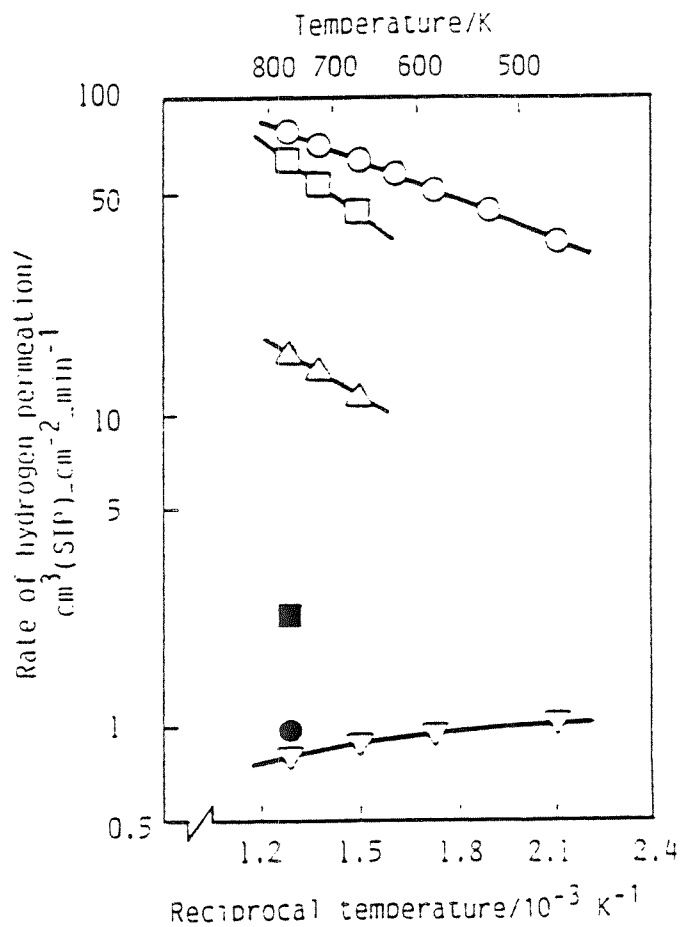


Fig. 9. Comparison of the rate of hydrogen permeation through various membranes: (o) Pd-Ag (23): porous alumina composite membrane (thickness of film 5.8 μm); (\square) Pd: porous alumina composite membrane (4.5 μm); (Δ) Pd: porous glass composite membrane (20 μm); (∇) porous Vycor glass (mean pore size 4 nm); (\bullet) reported value for commercially obtainable Pd membrane (thickness 150 μm); (\blacksquare) reported value for commercially obtainable Pd-Ag alloy membrane (150 μm).

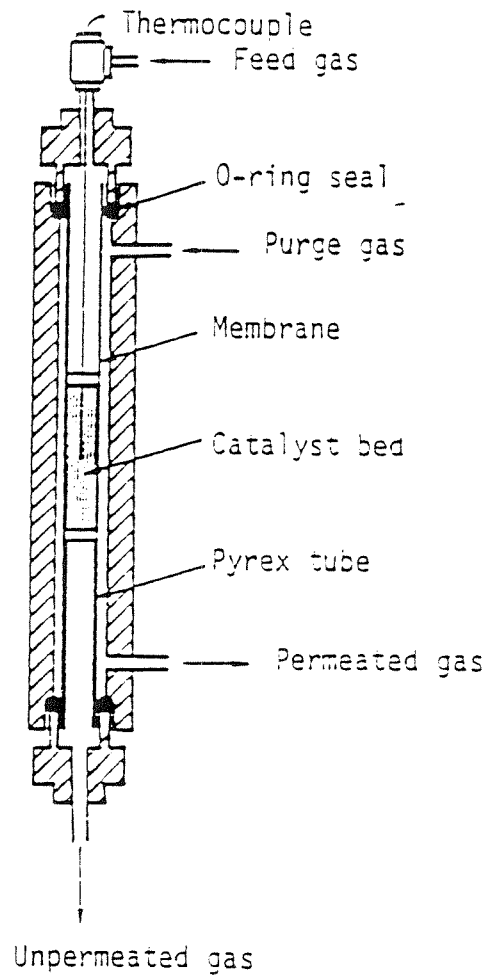


Fig. 10. Pd/porous glass membrane reactor.

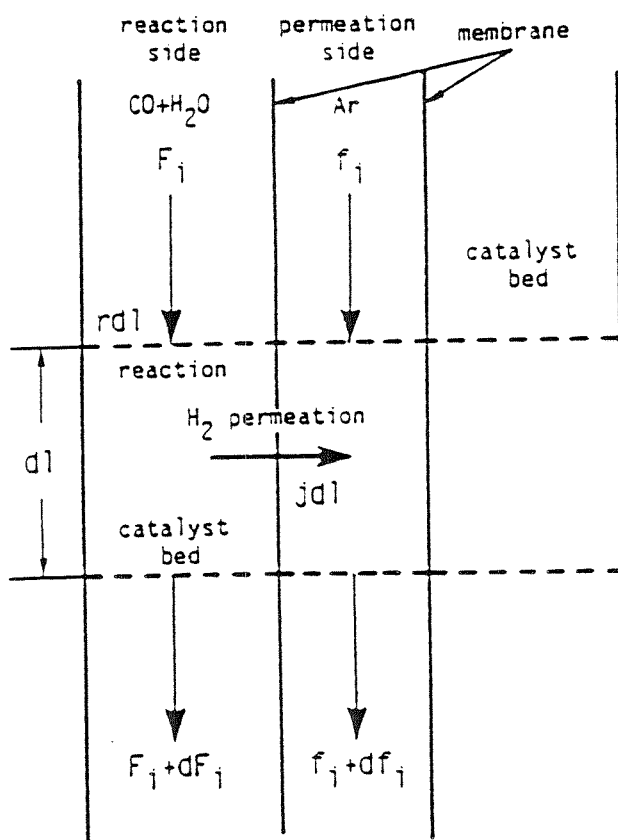


Fig. 11. Flow model for reaction and permeation in a palladium membrane reactor.

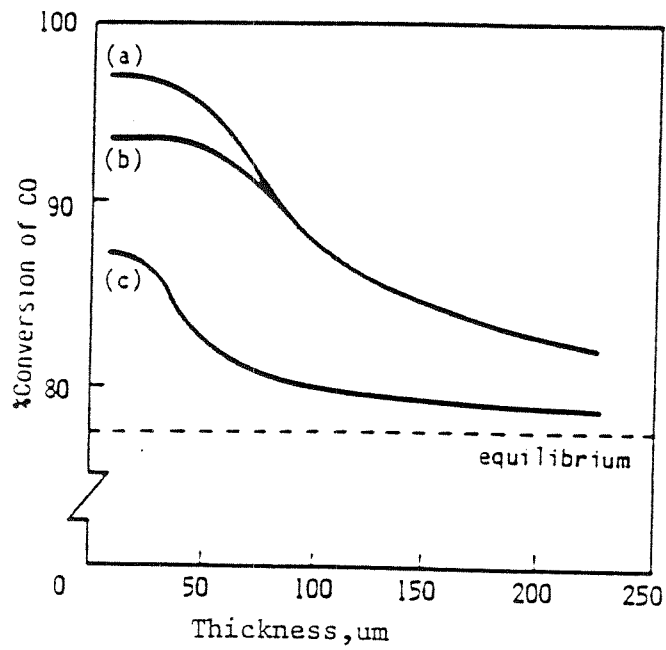


Fig. 12. Conversion of carbon monoxide as a function of palladium thickness. Feed rate of CO: (a) 25, (b) 25 and (c) 100 cm³ (STP) min⁻¹. Flow rate of sweep argon: (a) 3200, (b) 400 and (c) 400 cm³ (STP) min⁻¹.

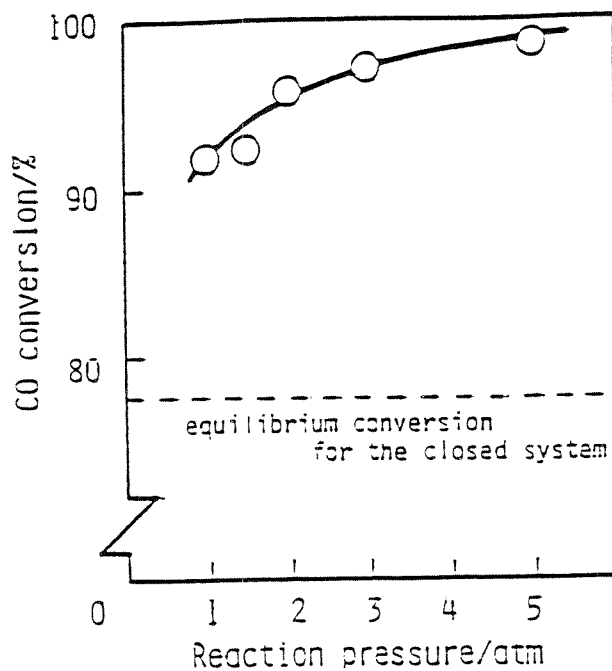


Fig. 13. Effect of reaction pressure on conversion of carbon monoxide.
Reaction conditions: catalyst (Girdler G-3), 3.0 g, temperature 400°C, H₂O/CO ratio 1, feed rate of carbon monoxide 25 ml min⁻¹.
Sweep argon: flow rate 400 ml min⁻¹, pressure 1 atm.

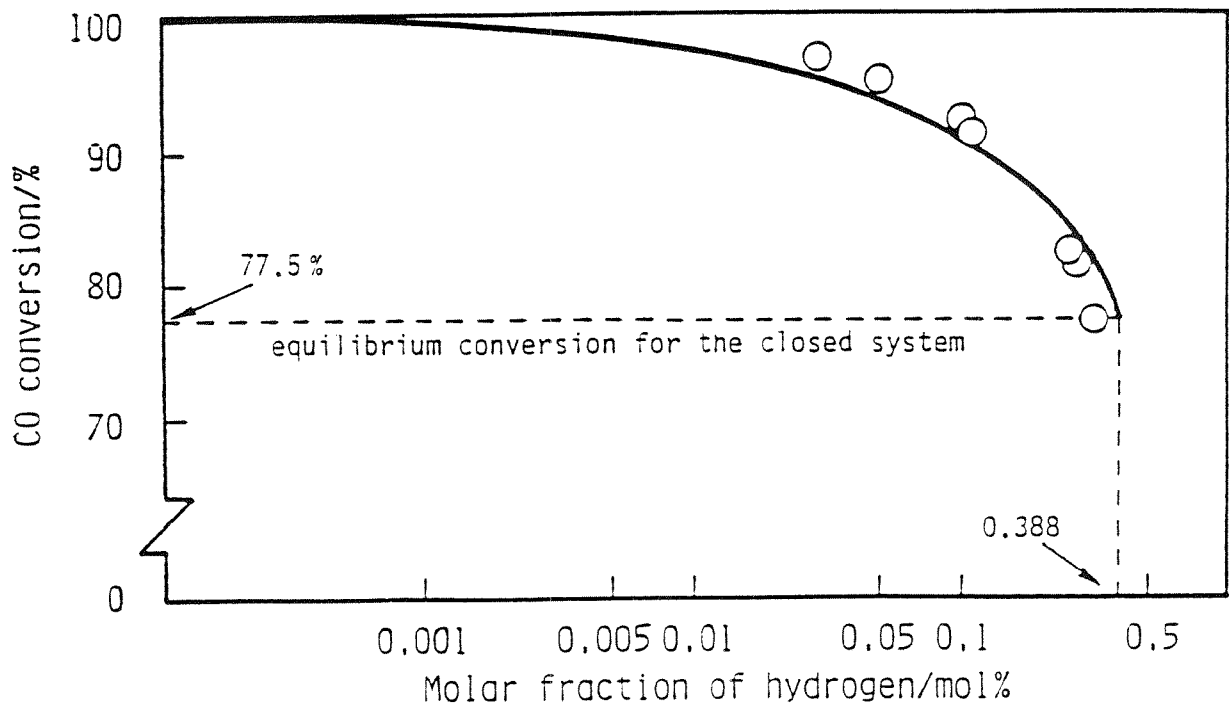


Fig. 14. Conversion of carbon monoxide as a function of the molar fraction of hydrogen at 400°C (o) experimental results, solid line represents theoretical values on the assumption of the chemical equilibrium ($K_p = 11.92$).

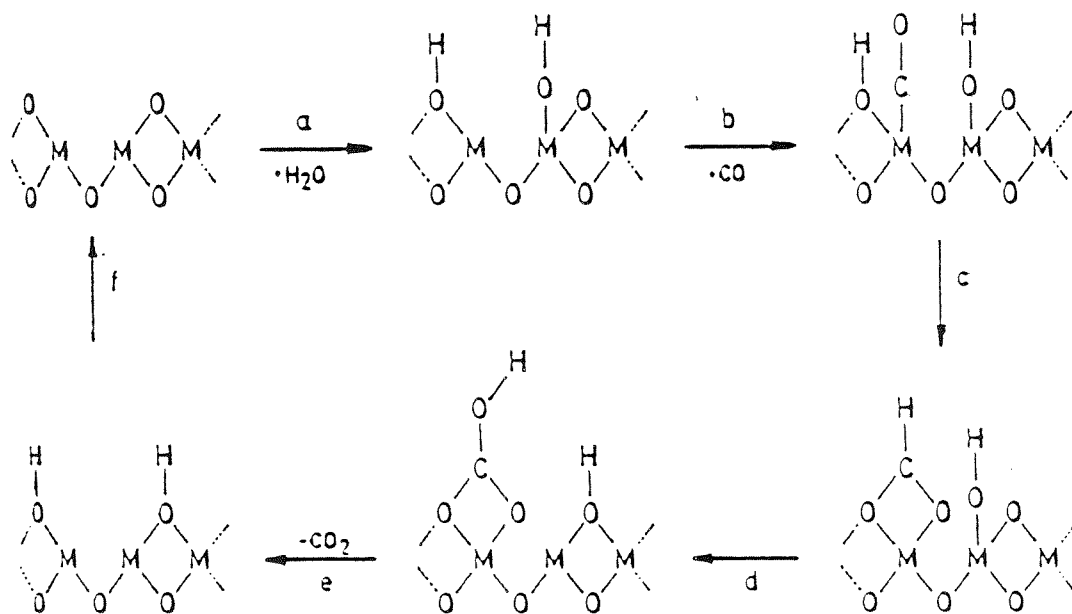


Fig. 15. Pathway for the water-gas shift reaction. (a) H_2O adsorbs on an anion vacancy and a surface oxygen; (b) CO adsorbs on anion vacancy; (c) adsorbed CO reacts with hydroxyl to form formate; (d) formate reacts to form bicarbonate; (e) CO_2 desorbs; (f) H_2 desorbs.

APPENDIX

Reaction mechanisms on the surface of the catalyst during the water-gas shift reaction

Two mechanisms are thought to be important for the water-gas shift reaction. On one hand there is the regenerative mechanism in which the catalyst surface is oxidized by H_2O , thereby releasing hydrogen gas, and subsequently reduced by CO resulting in the formation of CO_2 . This regenerative mechanism requires that the surface cations can change oxidation state which in the case of Fe should involve a fast electron hopping mechanism between the Fe^{2+} and Fe^{3+} states.

The second mechanism being proposed is an associative mechanism as shown in Fig. 15. In this pathway the activity of the catalyst in this shift reaction is largely determined by the oxidicity of the catalyst in combination with the support material. The mechanism involves a number of subsequent steps.

First H_2O adsorbs on an anion vacancy and a surface oxygen (step "a"). CO adsorbs on a coordinatively unsaturated cation to form a carbonyl species which then reacts with a hydroxyl group to generate a formate intermediate (steps "b" and "c"). In steps "d" and "e", the formate species react further with surface oxygen (hydroxyl groups) to form a carbonate (bicarbonate) which decomposes to give gaseous CO_2 and a surface oxygen (hydroxyl group). Finally, two hydrogen atoms combine to form H_2 returning the surface to its initial state (step "f").

Retwisch [12] suggests that the adsorption of CO is fast and reversible and that the rate determining step is the reaction occurring at the surface to generate a formate on a bicarbonate (step c and d). A metal oxide with strong acidity exhibits strong bands between the metal and the oxide which means that a formate or a bicarbonate is not readily formed leading to a low acidity of the catalyst. Also desorption of CO_2 from an acidic surface is a slow process. Carbon monoxide, which is a soft base, interacts strongly with soft acidic sites and therefore have high surface density on catalyst with low acidity.

From the arguments given above, it can be concluded that high acidity levels of the catalysts may be expected from $Zn,Cu/Al_2O_3$, Fe/Al_2O_3 and Fe/TiO_2 whereas low acidity is shown by materials like $Zn,Cu/SiO_2$ and Fe/SiO_2 .