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Separation of Hydrogen and Carbon Dioxide Using a Novel Membrane Reactor in Advanced Fossil Energy Conversion Process

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DISCLAIMER

ABSTRACT

Inorganic membrane reactors offer the possibility of combining reaction and separation in a single operation at high temperatures to overcome the equilibrium limitations experienced in conventional reactor configurations. Such attractive features can be advantageously utilized in a number of potential commercial opportunities, which include dehydrogenation, hydrogenation, oxidative dehydrogenation, oxidation and catalytic decomposition reactions. However, to be cost effective, significant technological advances and improvements will be required to solve several key issues which include: (a) permselective thin solid film, (b) thermal, chemical and mechanical stability of the film at high temperatures, and (c) reactor engineering and module development in relation to the development of effective seals at high temperature and high pressure.

In this project, we are working on the development and application of palladium and palladium-silver alloy thin-film composite membranes in membrane reactor-separator configuration for simultaneous production and separation of hydrogen and carbon dioxide at high temperature. From our research on Pd-composite membrane, we have demonstrated that the new membrane has significantly higher hydrogen flux with very high perm-selectivity than any of the membranes commercially available. The steam reforming of methane by equilibrium shift in Pd-composite membrane reactor is being studied to demonstrate the potential application of this new development.

A two-dimensional, pseudo-homogeneous membrane-reactor model was developed to investigate the steam-methane reforming (SMR) reactions in a Pd-based membrane reactor. Radial diffusion was taken into consideration to account for the concentration gradient in the radial direction due to hydrogen permeation through the membrane. With appropriate reaction rate expressions, a set of partial differential equations was derived using the continuity equation for the reaction system. The equations were solved by finite difference method. The solution of the model equations is complicated by the coupled reactions. At the inlet, if there is no hydrogen, rate expressions become singular. To overcome this problem, the first element of the reactor was treated as a continuous stirred tank reactor (CSTR). Several alternative numerical schemes were implemented in the solution algorithm to get a converged, stable solution. The model was also capable of handling steam-methane reforming reactions under non-membrane condition and equilibrium reaction conversions. Some of the numerical results were presented in the previous report.

To test the membrane reactor model, we fabricated Pd-stainless steel membranes in tubular configuration using electroless plating method coupled with osmotic pressure. Scanning Electron Microscopy (SEM) and Energy Dispersive Xray (EDX) were used to characterize the fabricated Pd-film composite membranes. Gas-permeation tests were performed to measure the permeability of hydrogen, nitrogen and helium using pure gas. Some of these results are discussed in this progress report.

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EXECUTIVE SUMMARY

Inorganic and composite membranes are being considered as potential candidates for use in membrane-reactor configuration for effectively increasing reaction rate, selectivity and yield of equilibrium limited reactions. To investigate the usefulness of palladium-ceramic and palladium-stainless steel composite membrane in membrane-reactor configuration, we are investigating the steam reforming of methane by equilibrium shift for simultaneous separation and recovery of hydrogen and carbon dioxide. To have a better understanding of the membrane reactor, we developed a two-dimensional pseudo-homogeneous reactor model for steam reforming of methane by equilibrium shift in a tubular membrane reactor. Parametrically we studied the performance of the reactor and the simulation results show that under appropriate operating conditions, the membrane reactor outperforms the conventional packed-bed reactor. We also fabricated Pd-stainless steel composite membrane by electroless deposition coupled with osmotic pressure. From gas permeability study, it was observed that the membrane has excellent H_2-permselectivity.

INTRODUCTION

Inorganic membrane reactors allow simultaneous reaction and separation, and therefore offer the possibility of combining reaction and separation in a single operation at high temperatures to overcome the equilibrium limitations experienced in conventional reactor configurations. Such attractive features can be advantageously utilized in a number of potential commercial opportunities, which include dehydrogenation, hydrogenation, oxidative dehydrogenation, oxidation and catalytic decomposition reactions. However, to be cost effective, significant technological advances and improvements will be required to solve several key issues which include: (a) permselective thin solid film, (b) thermal, chemical and mechanical stability of the film at high temperatures, and (c) reactor engineering and module development in relation to the development of effective seals at high temperature and high pressure.

In our laboratory, we developed a new class of palladium-ceramic composite membranes by depositing thin-film palladium on microporous ceramic substrate. Laboratory tests at elevated temperature and pressure indicated that the new membrane has both high permeability and selectivity for hydrogen [1]. We believe this new membrane will be an excellent candidate for hydrogen separation and applicable in membrane-reactor configuration for separation of hydrogen by equilibrium shift when the reaction product (H_2) thermodynamically limits the equilibrium conversion. In IGCC application, the clean syngas or natural gas can be steam reformed to produce H_2 and CO_2 in an H_2-selective membrane reactor. Since, these reactions are thermodynamically equilibrium-limited, the membrane reactor offers an opportunity for H_2 separation and CO_2 capture in a single unit. This method will have several technological advantages over other hydrogen-purification methods, including the following:

- Reforming reaction is not limited by chemical equilibrium. As soon as product hydrogen is formed, hydrogen is transported across the membrane.
- Reforming and separation will be carried out in a single unit, thereby eliminating the need of hydrogen separation and recovery units.
- The membrane reactor-separator is modular and compact in size.

We propose to use our newly developed membrane to study the water gas shift reaction and/or steam reforming of methane in a membrane reactor-separator for concentration and recovery of H_2 and CO_2 simultaneously.

RESEARCH OJECTIVES

The objectives of this research are to:

1. Design and fabrication of membrane reactor using thin film Pd-Ag alloy composite membrane in tubular configuration.
2. Conduct water-gas shift reaction and/or steam reforming of methane experiments to study the equilibrium shifts and permeation characteristics.
3. Model the membrane reactor for water-gas shift reaction and steam reforming of methane by equilibrium shift and validate the performance of the reactor.

FABRICATION OF PD-STAINLESS STEEL MEMBRANE

In recent years, there has been a growing interest in developing hydrogen-selective inorganic membrane for hydrogen separation, aimed at capitalizing the membrane selectivity in membrane reactor-separator configuration to enhance productivity of equilibrium-limited reactions, there is still a great deal of technical challenges that needs serious research efforts. The preparation of hydrogen selective palladium membrane that has high hydrogen flux and good thermal and mechanical stability is the major challenge that is being researched and investigated at laboratory scale. In this section, the fabrication of palladium membrane on porous stainless steel substrate (inside and outside surface) using electroless plating method combined with osmosis that we have developed in our lab is being discussed.

Electroless plating is based on the controlled autocatalyzed decomposition or reduction of metallic salt complexes on substrate surfaces. This method has several advantages over other deposition processes:

a) Both conducting (metal) and non-conducting (ceramic, polymer) surfaces can be coated
b) Uniform, thin dense films can be formed on bodies with complex shape
c) Relatively simple apparatus is required
d) The method is relatively inexpensive

In the lab palladium was deposited first on the inside surface of the asymmetric microporous stainless steel (SS) tubes purchased from Mott Metallurgical corporation. The inside and outside diameter of the SS tubes are ¼ and 3/8 inch, respectively. The average pore size of the tube is 0.2μm. The tubes purchased in lengths of 12 inch were first cut to the desired length of 2.5-4.0 inch using diamond saw. Several samples have been prepared changing some parameters such as pump speed, hydrazine concentration etc. All the samples were prepared according to the following three basic steps: (a) Substrate cleaning, (b) Sensitization and activation, and (c) Electroless plating.

The compositions of the sensitization and activation solutions along with the treatment conditions are given in Table 1. The sensitization and activation steps reduce the induction period of the palladium deposition, promotes complete coverage of the surface and improves coating quality. Sensitization is the adsorption of a reducing agent on the target surface and activation occurs when the catalytic material is adsorbed on the substrate. The oxidation/reduction mechanism for this step is:

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^{0}$$

Table 1: Composition of Sensitization and Activation Solutions

	Sensitization	Activation
Solute	$SnCl_2$	$PdCl_2$
Concentration	1.2 g/l	0.1 g/l
HCl (37%)	2.5 ml/l	2.5 ml/l
Temperature	Room temperature	Room temperature
Duration	~ 5 min	~ 5 min

Electroless plating is defined as the deposition of metallic coating by a controlled autocatalytic chemical reduction that is catalyzed by the metal or alloy being deposited. Plating was performed combined with osmosis that was originally developed by Yeung & Christiansen, 1999 [2]. Osmosis is the spontaneous flow of solvent, from a dilute to a more concentrated solution, when a suitable membrane separates the two liquids from each other. For osmosis to occur, the membrane should be semipermeable, i.e. allow free passage of the solvent but not of the dissolved solute. The composite membrane was prepared using a plating bath that contained EDTA stabilized palladium metal complex with hydrazine as reducing agent and ammonia to stabilize the bath and maintain the pH value. Table 2 shows the plating bath composition and the plating conditions. The palladium films were deposited on the inside surface of the metal tube by circulating the plating solution through the SS tube using a peristaltic pump. The experimental setup is shown in Figure 1. The osmotic solution used for this experiment is a high molecular weight polyethylene glycol (PEG) solution.

Table 2: Typical Pd electroless plating bath composition

Component	**Concentration**
$PdCl_2$ (99.9 % metals basis, Pd content 59.86%)	5 g/l
Na_2EDTA.	70 g/l
NH_4OH (28%)	500 ml/l
N_2H_4 (95% min)	10 ml/l
pH	10
Temperature	60 ^oC

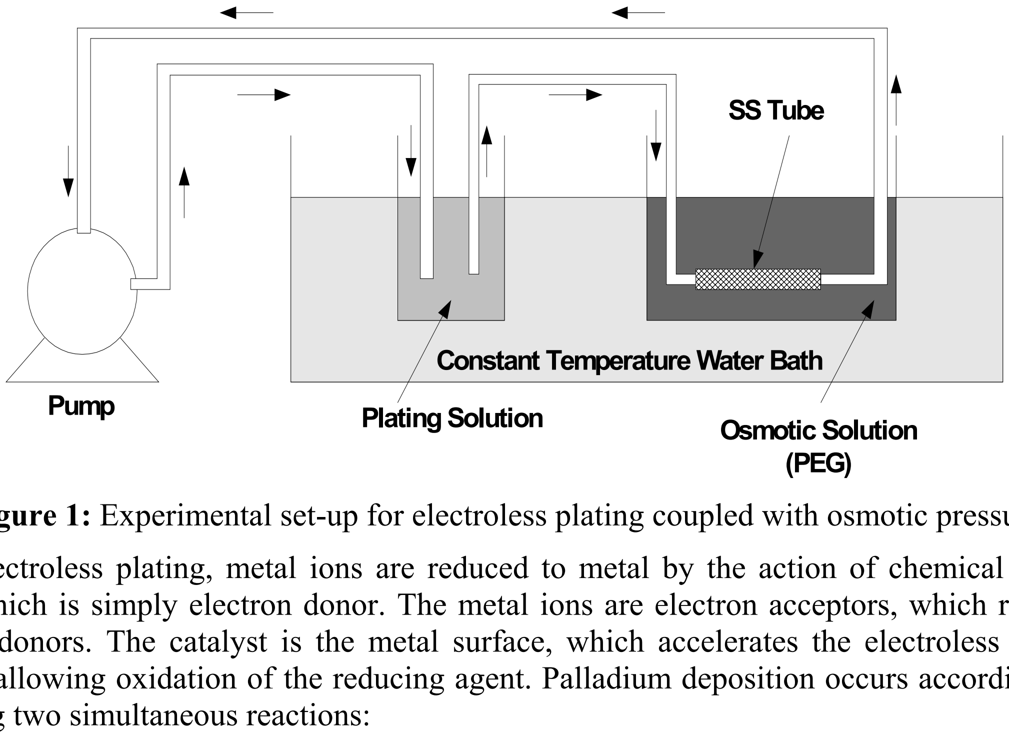


Figure 1: Experimental set-up for electroless plating coupled with osmotic pressure

In electroless plating, metal ions are reduced to metal by the action of chemical reducing agent, which is simply electron donor. The metal ions are electron acceptors, which react with electron donors. The catalyst is the metal surface, which accelerates the electroless chemical reaction allowing oxidation of the reducing agent. Palladium deposition occurs according to the following two simultaneous reactions:

Anodic reaction: $N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$

Cathodic reaction: $2Pd^{2+} + 4e^- \rightarrow 2Pd^0$

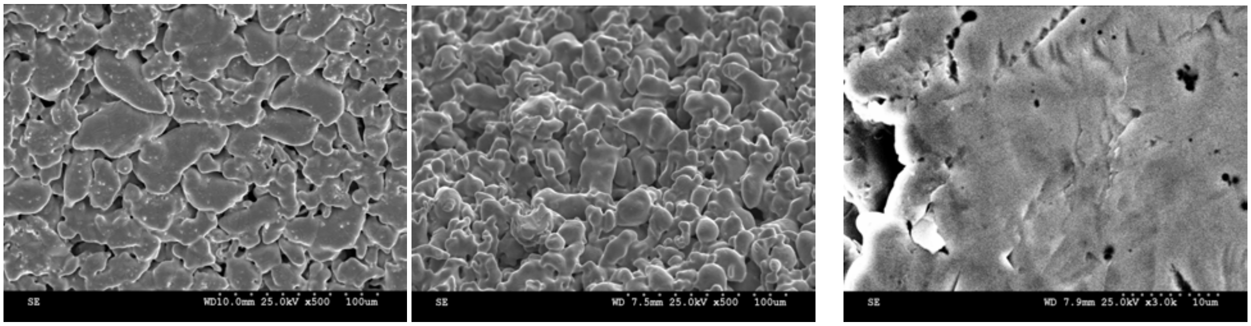
Autocatalytic reaction: $2Pd^{2+} + N_2H_4 + 4OH^- \rightarrow 2Pd + N_2 + 4H_2O$

The cathodic deposition of palladium catalyzes the anodic oxidation of hydrazine thus resulting in an autocatalytic process. Preseeded palladium nuclei on the substrate at the sensitization/activation step reduce the induction period of the autocatalytic process at the beginning of the deposition.

RESULTS AND DISCUSSIONS

In this work, a thin film palladium-stainless steel composite membrane was developed using electroless deposition technique. We investigated Pd-film deposition on both inside and outside surface of the stainless steel membrane. Effect of different parameters on the deposition process was examined. The surface morphology and microstructure of the composite membrane were also examined. The gas permeation behavior of the composite membrane was investigated at different temperature and pressure [3].

Figure 2(a), 2(b) and 2(c) show SEM micrographs of the inside surface and cross-sectional image of a SS tube. The average pore size is about 0.2μm. The SEM images show that the surface morphology of stainless tube is significantly different from inside to outside surface. Outside surface appear more compact than the inside surface.



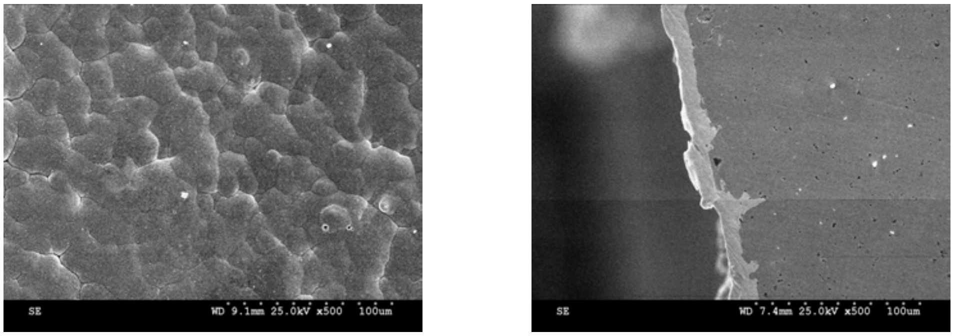
(a) (b) (c)

Figure 2: SEM of Stainless Steel tube, (a) Inside surface, (b) Outside surface, and (c) cross-sectional view.

The SEM of the Pd-film on the inside surface of the stainless steel tube is shown in Figure 3(a) and the penetration of the Pd into the pores is shown by the cross-sectional view in Figure 3(b). Although the coverage of the Pd-film visually appears adequate, but the cross-sectional view shows that the penetration through pores is not that great. The Pd-film thickness was estimated by weight-gain method to be about 10 μm thick.

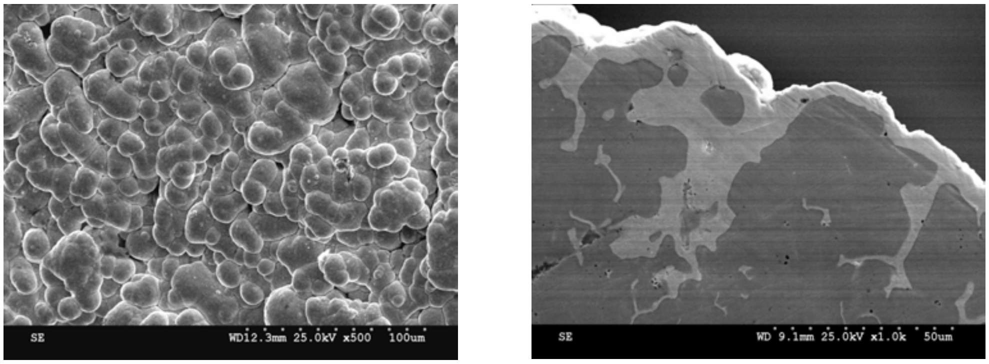
In Figure 4(a), the SEM image of the Pd-film deposited on the outside surface of stainless steel tube is shown. The penetration of the Pd-film through the pores is shown in Figure 4(b) as cross-sectional view. Comparing Figures 3(a,b) and 4(a,b), it appears that outside plating is superior compared to the inside surface. This is probably due coarse inside surface of the stainless steel tube. The Pd-film thickness on the outside surface was to be about 20 μm thick.

The membrane samples were further characterized by EDX analysis. EDX analysis was conducted to determine the elemental composition of the deposited Pd-film. Typical EDX analysis result is shown in Figure 5. Analysis confirmed the deposition of pure palladium on the surface of microporous stainless steel tube surface.



(a) (b)

Figure 3: SEM images of electroless deposited Pd-film, (a) On inside surface, and (b) Cross-sectional view of the Pd-film penetration through pores



(a) (b)

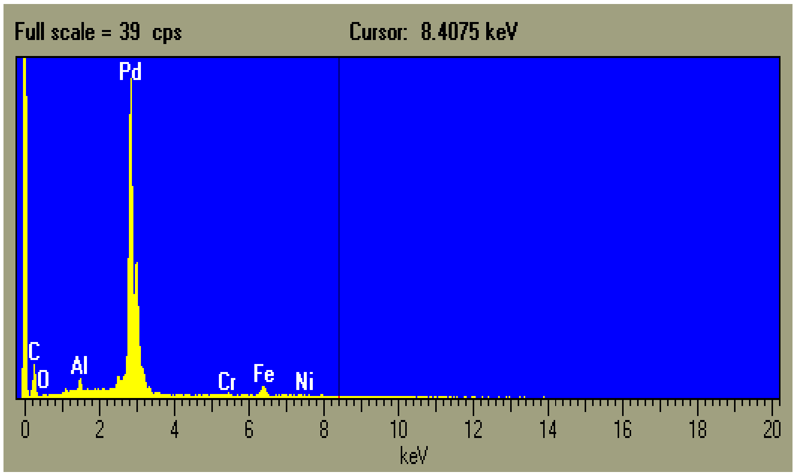
Figure 4: SEM images of electroless deposited Pd-film, (a) On outside surface, and (b) Cross-sectional view of the Pd-film penetration through pores

For the hydrogen permeation study, a 18μm thick Pd/SS membrane (corresponding to calculated weight gain of 21.22 mg/cm^2) was used. The effective membrane surface area was 18.0 cm^2). Gas permeability experiments were performed for three different pure gases: hydrogen, nitrogen and helium. Experiments were conducted at five different temperatures (325 to 450 ºC and eleven different pressures differentials (7.5 to 50 psi).

Figure 6 shows the dependency of the hydrogen permeation flux on the transmembrane pressure difference for different temperatures. The value of hydrogen pressure exponent, n was found to be 0.650, determined by regression analysis. The regression coefficients were found around 0.989 for all temperatures tested. For a given transmembrane pressure differential, hydrogen flux increases with increasing temperature. On the other hand, for nitrogen and helium with increasing temperature corresponding fluxes decrease to certain extent.

In Figure 7, the selectivity of hydrogen over nitrogen is shown for the same membrane as function transmembrane pressure differential over a temperature range of 325 to 450 ºC. The data show that the Pd-SS membrane has excellent perm-selectivity for hydrogen. Further, the H_2-

selectivity increases with increasing temperature. This makes the new membrane an excellent candidate for high temperature hydrogen separation applications.



Element	Spect. Type	Element %	Atomic %
Cr K	ED	0.61	1.20
Fe K	ED	3.78	6.91
Ni K	ED	0.17	0.29
Pd L	ED	95.44	91.59
Total		100.00	100.00

Figure 5: EDX analysis of Pd-film on microporous stainless steel tube

CONCLUSIONS

By electroless deposition, coupled with osmotic pressure we deposited thin Pd-film on microporous stainless steel tube. Because of different surface morphology, the deposited Pd-film on the inside and out side surface of the tube appears different both in SEM analysis and also in film penetration in the pores. Pd-film can be deposited easily on the outside surface compared to the inner surface. From limited permeability tests of hydrogen, nitrogen and helium, it was found that the new membrane has excellent hydrogen permeability and favorable hydrogen selectivity. Both hydrogen permeability and selectivity increases with increasing temperature for a given operating pressure. This characteristic makes the new membrane an excellent candidate for hydrogen separation at elevated temperature.

REFERENCES

1. Ilias, S., Su, N., King, F.G, and Udo-Aka, U.I., *Sep. Sci. & Tech.*, **32** (1-4), 487 (1997).
2. Yeung, K.L., and Christiansen, S.C., *J. Meb. Sci.,* **159**, 107 (1999).
3. Ahmed, S.J., Fabrication and Characterization of Pd-Stainless Steel Composite Membrane for Hydrogen Separation, MS Thesis, North Carolina A&T State University (2003).

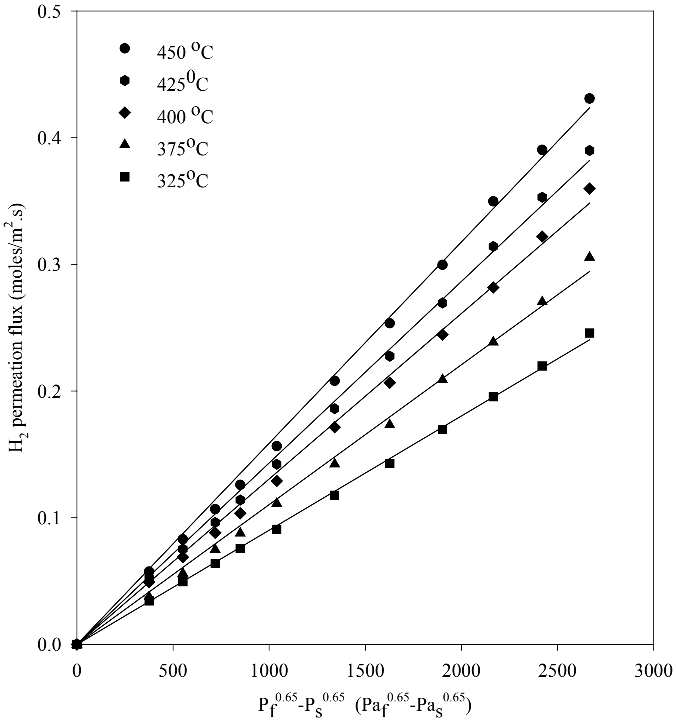


Figure 6: Hydrogen permeation flux through a 18 μm Pd/SS composite membrane as a function of the driving force for permeation. Temperature was decreased from 450°C to 325°C.

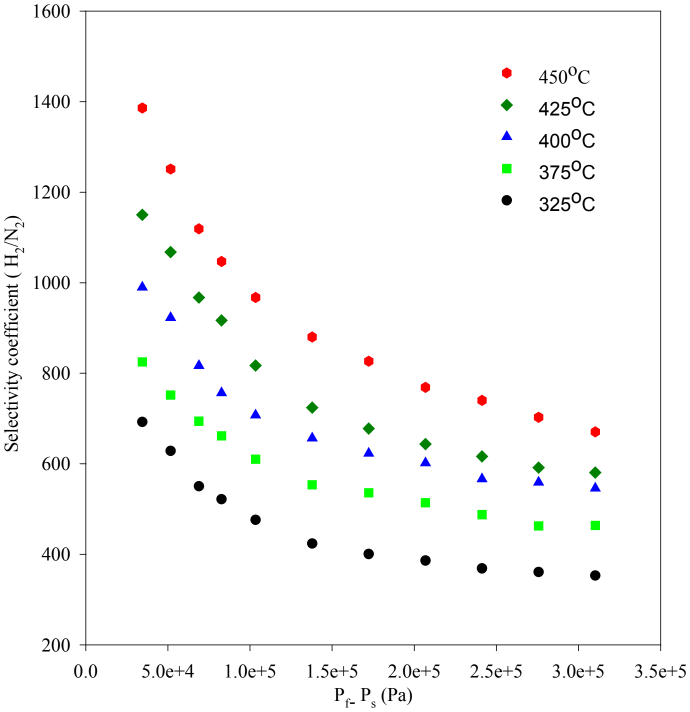


Figure 7: H_2/N_2 selectivity as a function of the pressure difference at different temperatures.