

The Effect of Humidity on the Durability of Inorganic Membranes

Yunfeng Gu, Byeong-Heon Jeong, Ken-Ichiro Sotowa and Katsuki Kusakabe[†]

Department of Applied Chemistry, Kyushu University, Fukuoka 812-8581, Japan

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Abstract—Porous oxide membranes of γ -alumina, zirconia and silica were prepared on porous α -alumina tubes by sol-gel processes. γ -Alumina and zirconia membranes impregnated with platinum were also prepared. The permeation properties of these membranes were investigated by using unary and binary feeds of H_2 and CO_2 at 423 K. After permeation for 5 h with humidification at a concentration of 3 mol%, no large changes were found for the zirconia and γ -alumina membranes, but the permeances to H_2 and CO_2 for the silica membrane were decreased by 10-20%. A 70-h exposure to humidified feeds showed that the zirconia- and γ -alumina-based membranes were more resistant than the silica membrane. The decrease in H_2 permeance was only 5% for the zirconia-based membranes and 17.4% for the silica membrane. The Pt-loaded γ -alumina membrane remained defect-free after one-month of exposure to the humidified feeds at 423 K.

Key words: Inorganic Membrane, Permeation, Moisture, Stability, Sol-Gel

INTRODUCTION

A variety of porous membranes have been developed and applied to gas separation [Uhlhorn et al., 1992; Morooka and Kusakabe, 1999; Ismail and David, 2001; Hasegawa et al., 2002]. In most studies, permeation properties are determined in a water-free atmosphere, even though water vapor is often present in gas feeds of actual separation processes. When mesoporous or microporous membranes are used for humidified feeds at low temperatures, water is condensed in the pores, and, as a result, permeances to noncondensable gases decrease.

Pan et al. [1999] reported that the O_2 permeances of a γ -alumina (Al_2O_3) membrane with a pore size of 4 nm decreased from $6.5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $1.5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at room temperature, in the presence of water at relative humidities of 20-80%. Poshusta et al. [2000] exposed SAPO-34 membranes to a humidified CO_2/CH_4 mixture at 300 K for 6 h. This treatment decreased the permeation fluxes approximately by one order of magnitude. When the membrane was dried at 473 K overnight, however, the fluxes returned to their initial values. In addition, some of the materials used in microporous membranes are not always stable against water vapor. It is well known that porous silica (SiO_2) easily undergoes densification upon exposure to water vapor at elevated temperatures. The densification involves the formation of Si-O-Si bonds from the silanol groups (Si-OH) via catalysis by water, leading to the shrinkage of pores [Iler, 1979]. It was reported that porous silica membranes prepared by chemical vapor deposition, when exposed to moisture at 873 K for several hours, lost 50% or more of their permeabilities [Tsapatsis and Gavalas, 1994; Morooka, 1995; Wu et al., 1994; Ioannides and Verykios, 1996].

Porous membranes which are made of zirconia (ZrO_2), γ -alumina and silica are commonly used for gas separation [Uhlhorn et al., 1992; Gu et al., 2001a; Cooper and Lin, 2002; Kusakabe et al.,

1999; Morooka and Kusakabe, 1999]. Metal-loaded zirconia and γ -alumina membranes are used for separation, as well catalysis, in applications to membrane reactors for the production of hydrogen as a fuel for polymer electrolyte membrane fuel cell at the temperature of 100-300 °C [Gu et al., 2002; Chai et al., 1994; Hasagawa et al., 2002]. However, information on the stability of porous membranes in the presence of water is lacking. In this study, therefore, the influence of humidity on gas permeation properties of such membranes was investigated.

EXPERIMENTAL

1. Zirconia and Pt-loaded Zirconia Membranes

Zirconia membranes were prepared by the dip-coating of a stable colloidal sol on a porous α -alumina support tube (supplied by NOK Corp., Japan; outer diameter=2.1 mm; inner diameter=1.7 mm; pore size=110-180 nm) [Gu et al., 2001a]. A zirconia sol was prepared by mixing 0.02 mol zirconium propoxide (70 wt% in 1-propanol), 0.24 mol 1-propanol, 0.005 mol 1,5-diaminopentane, and 0.08 mol glacial acetic acid. Nitric acid was added dropwise until the sol returned to a clear state. The sol was then dip-coated on a porous α -alumina support tube and dried overnight in ambient air. The tube was heated in air at a rate of 1 K min^{-1} , and the gel was calcined at 673 K for 1 h. This dipping-firing process was repeated for a total of five times. The membrane obtained was denoted as Z673. A Pt-loaded zirconia membrane was prepared by exposing membrane Z673 to an H_2PtCl_6 solution of 0.10 mol L^{-1} for 30 min, followed by calcination at 623 K. This process was repeated three times. The resulting membrane is denoted as PtZ623.

2. γ -Alumina and Pt-loaded γ -Alumina Membranes

γ -Alumina membranes were prepared by the dip-coating of a stable colloidal boehmite sol on the porous α -alumina support tube. The boehmite sol was prepared by using procedures described by Yoldas [1975], and the concentration of the boehmite sol was 0.6 mol L^{-1} . Only the outer surface of the support was dipped in the sol for 10 s and dried overnight in air. It was then heated to 1,073 K

[†]To whom correspondence should be addressed.

E-mail: kusactf@mbox.nc.kyushu-u.ac.jp

at a rate of 1 K min^{-1} . This dipping-firing sequence was repeated for a total of three times. The membrane is denoted as A1073. A Pt-loaded γ -alumina membrane was also prepared by the same impregnation procedure for membrane PtZ623. The resulting membrane is denoted as PtA623.

3. Silica Membranes

A stable silica sol was obtained by using tetraethoxysilane (TEOS) as the silica source and methacryloxypropyltrimethoxysilane (MTMS) as the so-called template. After mixing 0.108 mol TEOS, 1.14×10^{-2} mol MTMS and 30 ml ethanol (99.8%) at 330 K in a nitrogen atmosphere and stirring for 2 h under reflux, a mixture of 0.614 g H_2O , 2.44 g hydrochloric acid (35.0–37.0%) and 33 mL ethanol (99.8%) was added dropwise followed by stirring for another 2 h. A silica membrane was prepared by dip-coating a colloidal silica sol on the γ -alumina membrane, A1073, with a dipping time of 5 min [Kim et al., 2001]. After drying overnight, the membrane was heated at 1 K min^{-1} and calcined at 873 K for 2 h. The drying-firing procedure was repeated for a total of three times. This silica membrane is denoted as S873.

4. Preparation of Powders

Stable ZrO_2 , $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 sols, respectively, were cast on glass plates and dried in air at room temperature. The gels were recovered from the glass plates, powdered with an agate mortar, and then calcined at the temperatures used for the preparation of the corresponding membranes, Z673, A1073 and S873. Pt-loaded zirconia and γ -alumina powdered samples were obtained by using the H_2PtCl_6 solution with the same impregnation-calcination procedure adopted for membranes PtZ623 and PtA623. The resulting powdered samples are referred to with the same denotations as for their membranes.

5. Characterization

Pore size, pore size distribution, pore volume and surface area of the powdered samples were determined from sorption isotherms by using nitrogen and argon (Micrometrics, ASAP 2000 and 2010). Platinum loadings (wt%) of samples PtA623 and PtZ623 were determined by EDX (Kevex Delta Class). Fracture surfaces of the membranes were observed by scanning electron microscopy (SEM, Hitachi S-5200).

Table 1. Dry and single-component permeances of membranes at 423 K

Membrane	Code	Permeance $\times 10^8$ [$\text{mol Pa}^{-1}\text{s}^{-1}\text{m}^{-2}$]			Ideal selectivity	
		H_2	N_2	CO_2	H_2/N_2	H_2/CO_2
$\gamma\text{-Al}_2\text{O}_3$	A1073	1030	264	214	3.90	4.81
ZrO_2	Z673	529	105	83.7	5.04	6.32
Pt- $\gamma\text{-Al}_2\text{O}_3$	PtA623	16.8	2.88	2.23	5.83	7.53
Pt- ZrO_2	PtZ623	92.4	14.8	9.15	6.24	10.1
SiO_2	S873	8.12	0.756	1.51	10.7	5.38

The permeation properties of the oxide membranes were determined at 423 K, using single component H_2 and CO_2 and binary mixtures thereof. The H_2 mole concentration in the binary mixture was fixed at 75%, unless otherwise noted. Argon was used as the sweep gas on the permeate side. The total pressure on the feed and permeate sides was maintained at atmospheric pressure. Prior to the permeation tests, Pt-loaded membranes were exposed to H_2 at 523 K for 2 h.

The durability tests of the membranes in the humidified feeds were carried out at 423 K. A feed containing 3 mol% of water vapor was introduced for a prescribed period, and the supply of water vapor was temporarily stopped in order to determine gas permeances. The permeances were then determined after the membrane was stabilized by introducing the dry feed for 1 h.

RESULTS AND DISCUSSION

Table 1 shows the permeances to dry and single-component H_2 , N_2 and CO_2 at 423 K for membranes A1073, Z673, PtA623, PtZ623 and S873. The ideal H_2/N_2 and H_2/CO_2 selectivities for membranes A1073 and Z673 were close to the values expected by the Knudsen diffusion mechanism. This behavior is in agreement with the pore size distributions of the powdered samples, as shown in Fig. 1. Sample A1073 possessed a narrow pore distribution with a peak at approximately 5 nm. The zirconia sample Z673 had micropores

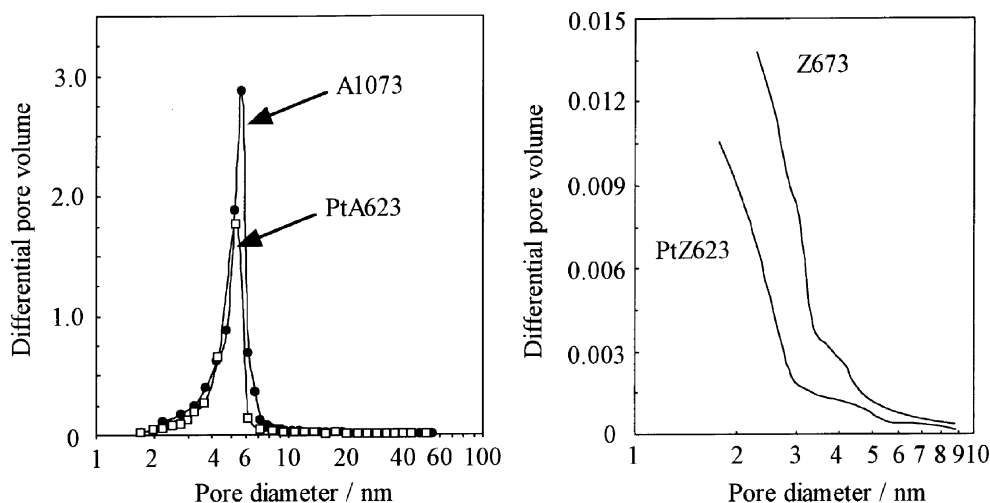


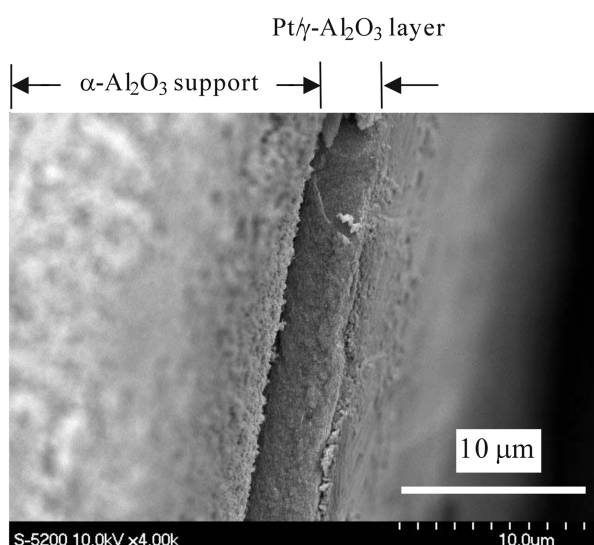
Fig. 1. Pore size distributions for powdered samples A1073, PtA623, Z673 and PtZ623.

Table 2. Pore structure data for powdered samples

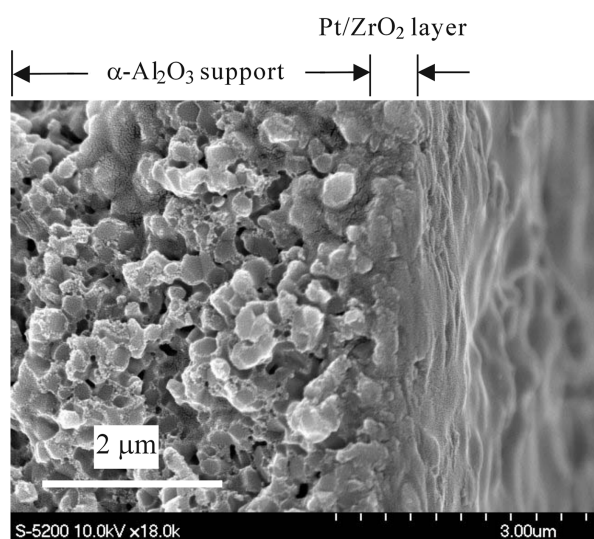
Sample	Code	Calcination temperature (K)	Average pore size (nm)	Pore volume (ml g ⁻¹)	Surface area (m ² g ⁻¹)	Pt-loading (wt%)
ZrO ₂	Z673	673	<2.0	0.008263	14.07	-
Pt-loaded ZrO ₂	PtZ623	623	<2.0	0.005757	3.705	4.26
γ-Al ₂ O ₃	A1073	1073	4.78	0.3109	259.9	-
Pt-loaded Al ₂ O ₃	PtA623	623	4.68	0.2576	220.0	13.72
SiO ₂	S873	873	0.86	0.03942	129.46	-

and mesopores. As shown in Table 2, the average pore size and pore volume of sample A1073 were larger than those of sample Z673. This corresponds to the findings that membrane A1073 exhibited higher permeances to H₂, N₂ and CO₂ than membrane Z673, as shown in Table 1. For both membranes A1073 and Z673, the Pt loading caused

an increase in H₂ selectivities by 20-60% and a decrease in permeances by 1-2 orders of magnitude. This behavior can be attributed to the decrease in pore size and pore volume after Pt loading, as shown in Fig. 1 and Table 2. The pore volumes of powdered samples PtA623 and PtZ623 were decreased by 17 and 30%, respectively, in comparison with powdered samples A1073 and Z673. Since powdered sample A1073 originally had a large pore volume, powdered sample PtA623 possessed a pore volume 45 times larger than that of powdered sample PtZ623.



(a) Membrane PtA623



(b) Membrane PtZ623

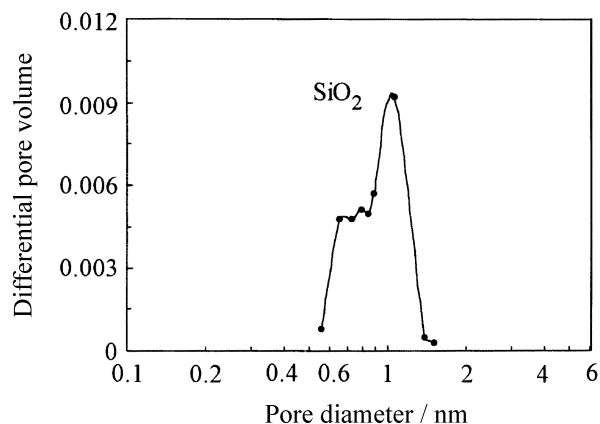
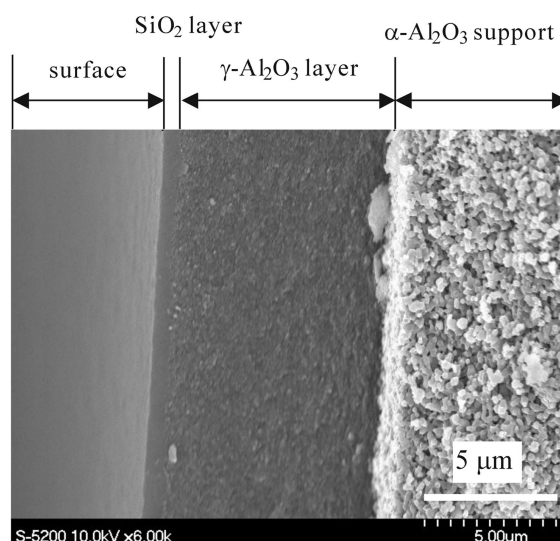
Fig. 2. SEM micrographs of the fractured surfaces of membranes PtA623 and PtZ623.**Fig. 3. Pore size distribution of powdered sample S873.****Fig. 4. SEM micrograph of the fractured surface of silica membrane S873.**

Fig. 2 shows SEM micrographs of the fractured surfaces of membranes PtA623 and PtZ623. For membrane PtA623, platinum was initially plugged in the pores and then formed a thin layer (approx-

imately 0.3 μm in thickness) on the top of the γ -alumina layer. For membrane PtZ623, however, this layer is not observed. This additional Pt layer led to a larger decrease in permeances for the γ -alu-

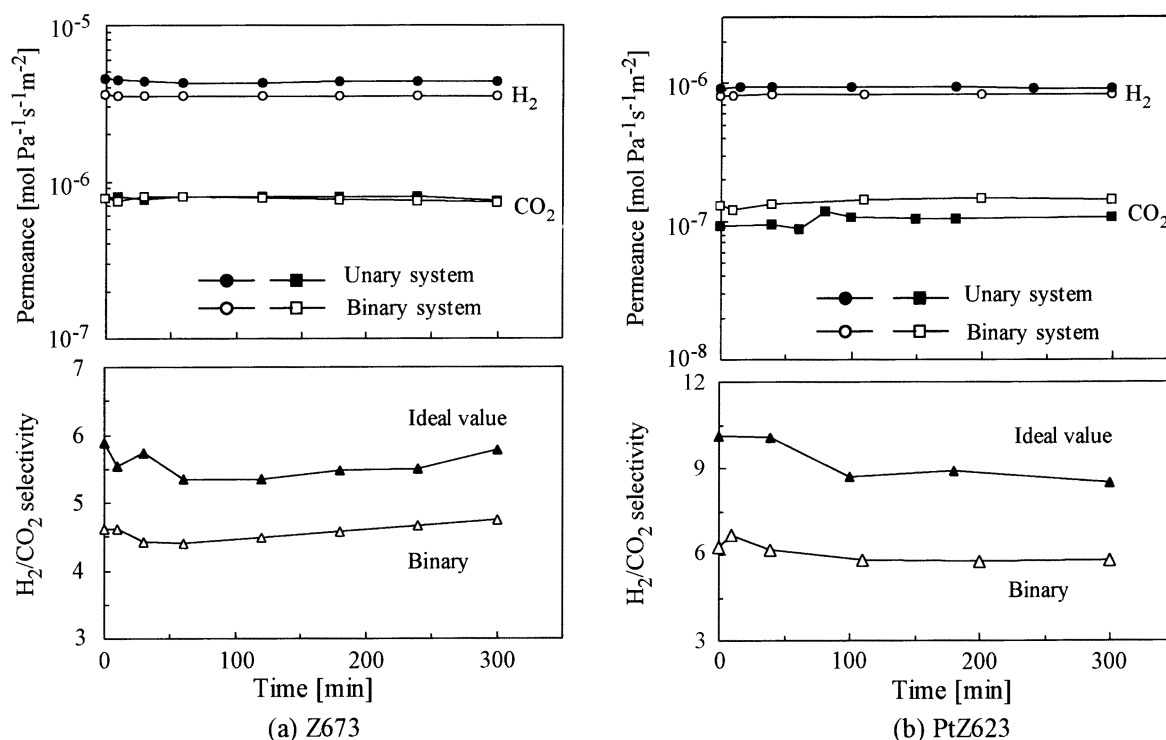


Fig. 5. Changes in H_2 and CO_2 permeation properties of the zirconia-based membranes as a function of exposure time at 423 K. (a) Membrane Z673 and (b) membrane PtZ623

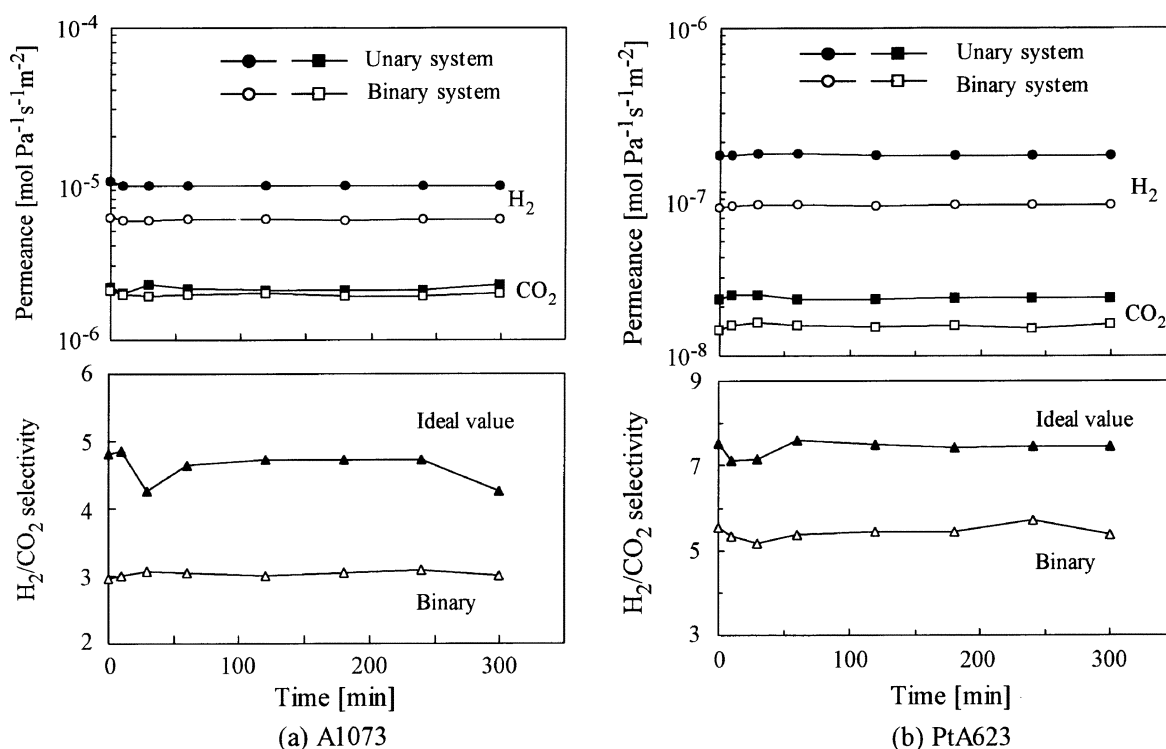


Fig. 6. Changes in H_2 and CO_2 permeation properties of the alumina-based membranes as a function of exposure time at 423 K. (a) Membrane A1073 and (b) membrane PtA623

mina-based membrane after Pt impregnation.

Fig. 3 shows the pore size distribution of powdered sample S873. The average pore size was 0.86 nm, which was much smaller than that of samples A1073 and Z673. This leads to lower H_2 and N_2 permeances and higher ideal H_2/N_2 selectivities for membrane S873, compared to membranes A1073 and Z673. The lower H_2/CO_2 selectivities can be attributed to the stronger adsorption of CO_2 in the SiO_2 pores. Fig. 4 shows an SEM micrograph of the fractured surface of membrane S873. The SiO_2 and $\gamma-Al_2O_3$ layers were 0.7 and 8 μm in thickness, respectively.

Fig. 5 shows changes in permeances for unary and binary feeds of H_2 and CO_2 at 423 K for membranes Z673 and PtZ623. The feed of water vapor had no substantial effect on the permeation properties of H_2 and CO_2 , although some small effects were observed. In the presence of water vapor, the H_2 permeances for the binary feed of H_2 and CO_2 were lower than those for the unary feed of H_2 . The CO_2 permeances were independent of the coexistence of H_2 . Thus the H_2/CO_2 selectivities were 20% and 30% lower, respectively, than the ideal selectivities for membranes Z673 and PtZ623. This was observed both in the absence and presence of water vapor. Slowly diffusing molecules generally decrease the diffusivity of fast diffusing molecules [Gu et al., 2001a; Guan et al., 2001].

Fig. 6 shows the H_2 and CO_2 permeation properties for unary- and binary-component systems at 423 K for membranes A1073 and PtA623. The water vapor had no effect on the permeation properties of membranes A1073 and PtA623. Due to the lower H_2 permeances for the binary system, the H_2/CO_2 selectivities were approximately 30% lower than the ideal values for these membranes.

Fig. 7 shows the variations in permeation properties for membrane S873 at 423 K for unary and binary feeds of H_2 and CO_2 . Due to the feed of water vapor, both H_2 and CO_2 permeances decreased, particularly in the initial period. The H_2/CO_2 selectivity data remained unchanged. This is in agreement with the results for silica-based membranes reported by Tsapatsis and Gavalas [1994]. After a 5-h exposure to water vapor, the H_2 and CO_2 permeances for membrane S873 decreased by 15%, which was higher than the value (5%) observed for the alumina-based and zirconia-based membranes shown in Figs. 5 and 6. The decrease in permeances for membrane S873 can be attributed to the change in the microstructure of silica [Tsapatsis and Gavalas, 1994; Morooka et al., 1995; Wu et al., 1994]. Porous alumina-based and zirconia-based membranes are more stable than silica membranes probably because Al-OH and Zr-OH groups are more resistant to hydrothermal densification than Si-OH groups.

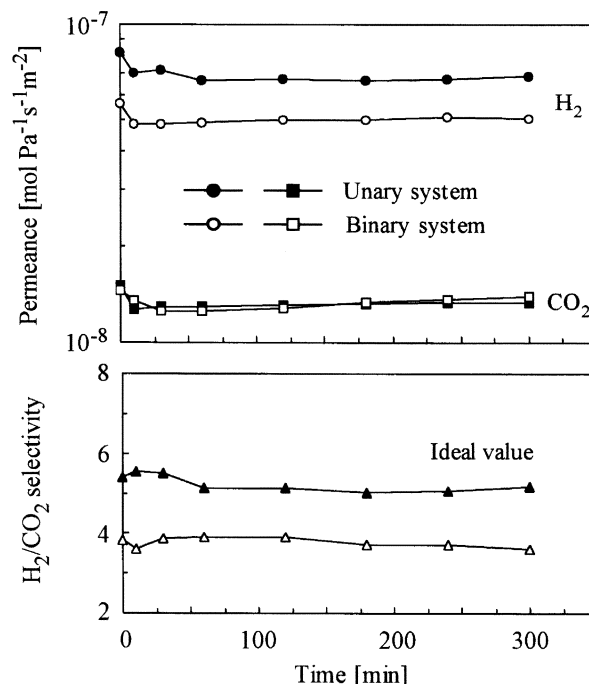


Fig. 7. Changes in H_2 and CO_2 permeation properties of the silica membrane (S873) as a function of exposure time at 423 K.

The membranes were further exposed to water vapor of 3 mol% at 423 K for 70 h, as shown in Table 3. Major changes were observed in the first 25 h. Membrane S873 showed the largest decrease in H_2 permeance, approximately 20%, after 70 h. The H_2 permeance increased by 4–5% for membranes PtA623 and PtZ623, while those for membrane A1073 and Z673 decreased by 7–10%. It can be assumed that impregnated platinum oxide, which had not been completely reduced by H_2 treatment at 523 K for 2 h, was gradually reduced during the permeation test.

CONCLUSIONS

Alumina-based ($\gamma-Al_2O_3$ and Pt-loaded $\gamma-Al_2O_3$) membranes, zirconia-based (ZrO_2 and Pt-loaded ZrO_2) membranes and silica membranes were prepared on porous support tubes. The permeation properties of these membranes were then evaluated for unary and binary feeds of H_2 and CO_2 , in the presence and absence of water vapor at a temperature of 423 K. After exposure to the feeds, which

Table 3. Fractional changes in permeances to single-component H_2 at 423 K during exposure to 3 mol% water vapor

Exposure time (h)	Original membranes						Pt-loaded membranes			
	A1073		Z673		S873		PtA623		PtZ623	
	Π	Change (%)	Π	Change (%)	Π	Change (%)	Π	Change (%)	Π	Change (%)
0	1030	-	529	-	8.12	-	16.8	-	92.4	-
5	972	-5.63	503	-4.91	6.85	-15.6	16.7	-0.60	92.4	0
15	964	-6.41	494	-6.62	6.72	-17.2	17.3	2.98	94.6	2.38
25	964	-6.41	493	-6.81	6.60	-18.7	17.6	4.76	94.4	2.16
40	941	-8.64	491	-7.18	6.52	-19.7	17.7	5.36	95.4	3.25
70	927	-10.0	491	-7.18	6.42	-20.9	17.6	4.76	96.0	3.90

Π : Permeance $\times 10^8$ [mol $Pa^{-1} s^{-1} m^{-2}$]

contained 3 mol% water vapor, the permeation properties of the alumina-based and zirconia-based membranes were unaffected. However, the H_2 and CO_2 permeances of the silica membrane suffered a decrease of 10–20%, although the H_2/CO_2 selectivity remained nearly unchanged. After a 70-h exposure to the humidified feeds, the H_2 permeance decreased by 10% for the alumina-based and zirconia-based membranes, and by 21% for the silica membrane. The reduction in permeances for the silica membrane was caused by hydrothermal densification during its exposure to water vapor. The tests indicate that the zirconia-based membranes had the best hydrothermal stability of the membranes tested. The Pt-loaded alumina membrane was crack-free after an exposure for a period of one month.

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