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EFFECT OF CHELATING AGENT 1,5-DIAMINOPENTANE ON THE MICROSTRUCTURES OF SOL-GEL DERIVED ZIRCONIA MEMBRANES

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ABSTRACT

Zirconia is more chemically stable than silica and γ-alumina, which are commonly used in the preparation of inorganic membranes. However, the hydrolysis of zirconia alkoxides, typical zirconia precursors, proceeds rapidly, leading to difficulties in preparing clear sols. Thus, an attempt was made to reduce the hydrolysis rate of zirconium propoxide by a ligand-exchange reaction with 1,5-diaminopentane (DAP). The availability of water was also reduced by the dropwise addition of glacial acetic acid, which produced an ester by reaction with the solvent, 1-propanol. The addition of DAP was effective in preparing zirconia with a narrow pore-size distribution and a high mesopore volume. DAP also decreased the phase transformation temperature of zirconia and had

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almost no effect on the micropore structures. The gas permeation properties of the prepared zirconia membranes were fundamentally controlled by the Knudsen diffusion mechanism.

Key Words: Zirconia; Sol-gel; Chelation; Esterification; Microstructure

INTRODUCTION

The sol-gel technique is widely used in the fabrication of porous ceramic membranes, which can be used for ultrafiltration and gas separation (1–3). Silica and alumina membranes (4–9) have been the most intensively investigated, and titania membranes have been also prepared (10,11). Zirconia membranes are more chemically stable than titania and γ-alumina membranes, but only limited information regarding their characterization has been published to date. Kim and Lin (12) showed that mesopores in zirconia membranes displayed less tortuousity than did those of γ-alumina membranes, which resulted in higher gas permeation fluxes for the zirconia membranes. Chang, Gopalan, and Lin (13) reported that large agglomerates were formed immediately after the addition of water. One of the reasons for the instability of a zirconia sol is the rapid rate of hydrolysis of zirconium alkoxide, which is commonly used as the precursor.

The hydrolysis rate of alkoxides can be controlled by chelation with ligand-exchanging reagents (14,15). Okubo et al. (16) prepared a stable zirconia sol from zirconium butoxide using triethanol amine as the chelating agent. Acetylacetone and diethanol amine were also used as chelating agents for zirconium and titanium alkoxides, respectively (10,17,18). Recently, Wu and Cheng (19) reported on attempts to control the hydrolysis rate of zirconium butoxide by controlling the feed rate of water, which was slowly released via the esterification between 1-butanol and glacial acetic acid. The sol, which was formed by the above procedure, was then used in the preparation of zirconia membranes. The average pore diameter of the membranes, which were obtained after calcination at 773 K, was 3.6 nm. However, further studies are needed to clarify the role of chelating agents in the formation of microstructures in zirconia membranes derived from sol-gels.

In the present study, we used 1,5-diaminopentane ($H_2N(CH_2)_5NH_2$, DAP), for the ligand exchange reaction, to control the hydrolysis rate of zirconium propoxide ($Zr(OCH_2CH_2CH_3)_4$, ZTP). The rate of water release was controlled by esterification between acetic acid and the solvent, 1-propanol. The effect of DAP was evaluated based on the nature of the microstructures as well as the gas permeance values of the resulting zirconia membranes.

EXPERIMENTAL

Preparation of Zirconia Sols

Figure 1 shows the procedure for the preparation of the zirconia sols. Hydrolysis was performed in the dry nitrogen atmosphere of a glove box.

1. 0.02 mol of ZTP (70% (wt) in 1-propanol, Gelest), 0.24 mol of 1-propanol (>99.5%, Wako), and 0–0.04 mol of DAP (Tokyo Kasei) were mixed. The molar ratio of DAP to zirconium propoxide is hereafter referred to as the DAP/Zr ratio. The mixture was stirred for 30 minutes, and 0.08 mol of glacial acetic acid (>99.7%, Wako) was then added, resulting in a clear solution. The stirring was continued, and the time at which the clear solution became cloudy was recorded as the precipitation time. Concentrated nitric acid was then added dropwise until the pH value of the solution reached approximately unity and the sol returned to a clear state.
2. A mixture of ZTP, 1-propanol, and DAP was prepared at a molar ratio of 4:96:1. A prescribed amount of acetic acid was then added to the mixture under continuous stirring, and the precipitation time was also recorded. The molar ratio of acetic acid to ZTP is hereafter referred as the acid/Zr value.

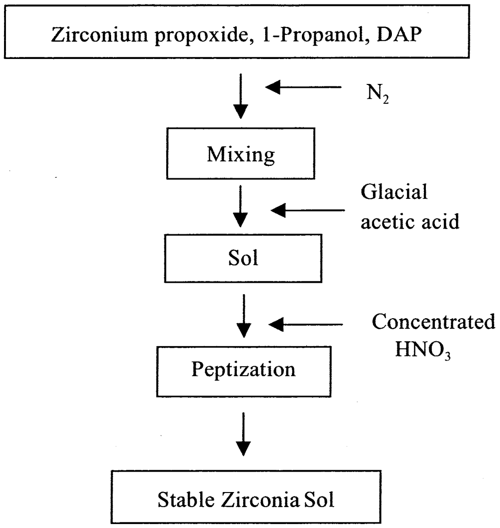


Figure 1. Procedure for the preparation of stable zirconia sols.

Calcination

Each zirconia sol was cast on a glass plate and dried in air at room temperature. Flakes were then recovered and pulverized with an agate mortar. The gel was then calcined at 773 K for 1 hour at a heating rate of 1 K/min. The zirconia sol was also coated on a porous α-Al_2O_3 support tube (supplied by NOK Corp, Japan; o.d. = 2.6 mm; inner diameter = 1.9 mm; pore size = 110–180 nm). The support tube, the lower end of which was closed, was dipped in the zirconia sol for 1 minute, withdrawn at a speed of approximately 7 mm/s, and dried overnight in ambient air. It was then calcined using the same procedure as was used for the flakes. This dipping-firing process was repeated 3 times.

Characterization

The calcined zirconia flakes were characterized by means of thermogravimetric analysis (TG) and differential thermal analysis (DTA). The phase structures of zirconia were determined by X-ray diffraction (XRD). The crystallite size was estimated using Scherrer's equation:

$$D = 0.89\lambda/(\mathrm{B}\cos\theta) \tag{1}$$

where D is the crystallite size; λ is the wavelength of Cu Kα radiation; θ is the Bragg angle; and B is the calibrated width of the diffraction peak at the half-maximum intensity. The pore size, surface area, pore volume, and pore size distribution of the calcined zirconia were calculated from nitrogen sorption isotherms measured with an adsorption porosimeter (Micrometrics, ASAP 2000). Permeation properties of the membranes were determined through the use of N_2, O_2, CO_2, CH_4, and iso-C_4H_{10}. Argon was used as the sweep gas.

RESULTS AND DISCUSSION

Stability of Zirconia Sols

Control of Hydrolysis Rate by the Ligand Exchange Reaction

To determine the effect of moisture in the glove box, we stirred a mixture of ZTP and 1-propanol without acetic acid. No precipitation was observed for 24 hours of stirring. This result showed that the influence of ambient moisture on the hydrolysis could be ruled out in the present study.

During the sol-gel process, the macromolecular network of zirconia is formed by the following reactions:

$$Zr(OR)_4 + H_2O \rightarrow Zr(OR)_3(OH) + ROH \tag{2}$$

$$\rightarrow Zr(OR)_2(OH)_2 + 2ROH \tag{3}$$

$$\rightarrow \mathrm{Zr(OR)\,(OH)_3} + 3\mathrm{ROH} \tag{4}$$

$$\rightarrow \mathrm{Zr(OH)_4} + 4\mathrm{ROH} \tag{5}$$

$$2\mathrm{Zr(OR)_3(OH)} \rightarrow \mathrm{(OR)_3Zr{-}O{-}Zr(OR)_3} + \mathrm{H_2O} \tag{6}$$

$$2\mathrm{Zr(OR)_2(OH)_2} \rightarrow \mathrm{(OR)_2(OH)Zr{-}O{-}Zr(OR)_2(OH)} + \mathrm{H_2O}, \text{etc.} \tag{7}$$

Reactions depicted in Eqs. (2–5) describe the hydrolysis, and Eqs. (6 and 7) describe the condensation. When the hydrolysis reactions (Eqs. 2–5) proceed at much faster rates than do the condensation reactions (Eqs. 6 and 7), precipitates of zirconium hydroxide may be formed. In the reverse case, the sol remains clear, as reported for silica sol (20). The hydrolysis rate can be decreased by the slow release of water that results from the esterification reaction between acetic acid and 1-propanol. As shown in Table 1, this procedure was effective in keeping the sol clear for 2.5 hours. Table 1 also shows the effect of DAP/Zr on the stability of the prepared sols. The precipitation time increased with increasing DAP/Zr values. When the amount of DAP was increased to DAP/Zr = 2.0 (200DZ), a gel was formed after 10 days. The result suggests that the hydrolysis rate was effectively reduced by the ligand exchange reaction between DAP and ZTP.

The hydrolyzed zirconia solution was then peptized with concentrated nitric acid, resulting in a clear sol. The clarity of the sol persisted for more than 4 months as a result of the electrostatic repulsion between sol particles, which were highly charged at such a low pH value. Because peptized sols 100AZ and 200AZ (Table 1) were very viscous, the sols prepared with DAP/Zr = 0.5 were used in subsequent experiments.

Control of Hydrolysis Rate by Esterification

The amount of water is critically important in the preparation of stable zirconia sols. In the present study, water was slowly released by esterification be-

Table 1. Effect of DAP/Zr on the Stability of Zirconia Sols

Sample	DAP/Zr	Condition of Sol	Precipitation Time (hours)	State After Peptization
0DZ	0	Clear	2.5	Clear sol
10DZ	0.1	Clear	4	
25DZ	0.25	Clear, light yellow	35	
50DZ	0.5	Clear, light yellow	80	
100DZ	1	Clear, yellow	100	Viscous sol
200DZ	2	Clear, yellow	240	

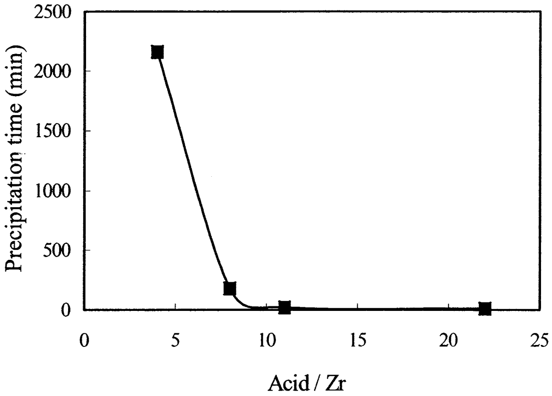


Figure 2. Effect of acid/Zr value on precipitation time.

tween 1-propanol and acetic acid. The amount of 1-propanol in the solution was fixed, and the amount of acetic acid was varied. When no acetic acid was added, as shown in Fig. 2, the solution remained clear because ZTP was not hydrolyzed. Under the condition of acid/Zr = 4.0, the sol still remained clear for approximately 40 hours. However, the sol turned cloudy only 10 minutes after the addition of acetic acid at acid/Zr = 21. The more acetic acid that was added, the more water was produced via the esterification reaction, and the hydrolysis proceeded more rapidly with accompanying precipitation.

Calcination

To determine the appropriate calcination temperature for the resulting zirconia gels, TG/DTA was performed in air. As shown in Fig. 3, the weight loss of sample 10DZ in the temperature range below 378 K is 14% and is due to the evaporation of physically adsorbed water and 1-propanol (boiling point = 370 K). The large exothermic peak observed near 523 K corresponds to a weight loss of more than 40% as determined by TG analysis and is attributed to the oxidation of nitro compounds, which are formed by the nitration of propanone acetate and nitric acid:

$$CH_3COOCH_2CH_2CH_3 + HNO_3 \rightarrow CH_3CH_2CH_2ONO_3 + CH_3COOH \quad (8)$$

The exothermic peak at 733 K is related to weight loss in the range of 513–653 K and can be explained by combustion of the organic matter. Because no obvious weight loss was observed at temperatures higher than 723 K, the calcination of zirconia membranes was completed below this temperature.

The tetragonal phase is the first to crystallize and is then transformed to the monoclinic phase at higher temperatures. Figure 4 shows the XRD patterns of zir-

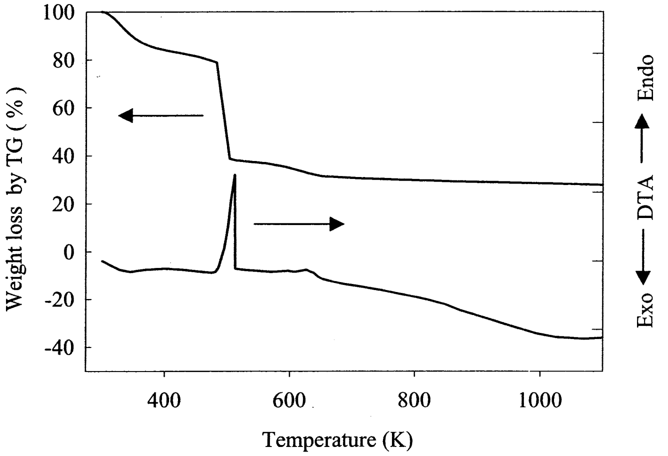


Figure 3. TG-DTA curves for a zirconia gel prepared with DAP/Zr = 0.10.

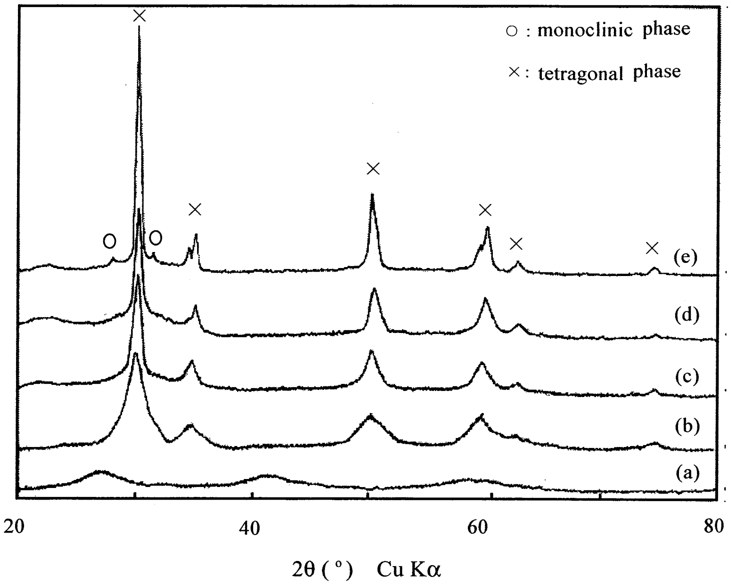


Figure 4. XRD spectra of zirconia samples: (a) dried gel (DAP/Zr = 0.50); (b) calcined (DAP/Zr = 0.50); (c) calcined (DAP/Zr = 0.25); (d) calcined (DAP/Zr = 0.10); and (e) calcined (DAP/Zr = 0).

Table 2. Effect of DAP/Zr on the Microstructures of Calcined Samples

Sample	DAP/Zr	Size by XRD (nm)	Size by BET (nm)	Agglomeration Degree
0DZ	0	22.4	191	8.55
10DZ	0.1	19.3	107	5.54
25DZ	0.25	15.3	70.8	4.63
50DZ	0.5	6.1	58.9	9.66

conia samples before and after calcination. Gel 0DZ, which was prepared without DAP addition, was amorphous prior to calcination. However, after calcination at 773 K, it was transformed to a tetragonal zirconia with a small fraction in the monoclinic phase. Only the tetragonal phase was found for flakes prepared from the sols with DAP. This finding suggests that the use of DAP decreased the phase transformation temperature. Figure 4 also shows that the addition of DAP broadened the peak, indicating that relatively fine crystallites were formed. As shown in Table 2, the crystallite size, as calculated from Scherrer's equation, was 15.3 nm for zirconia 25DZ, which was prepared from the sol with DAP/Zr = 0.25. This is smaller than the 20.8 nm reported by Kim and Lin (12) for yttria stabilized zirconia (YSZ) particles.

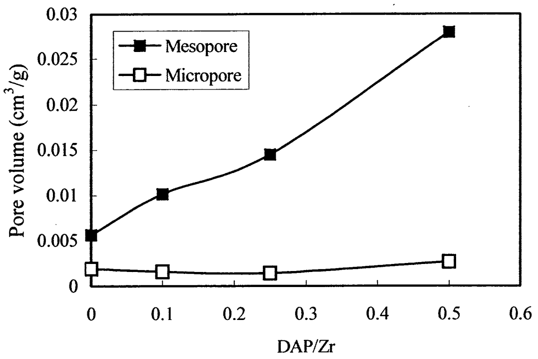
Microstructures

Because zirconia particles prepared by sol-gel process are mostly spherical (19), the average size can be calculated from the Brunauer, Emmett, and Teller (BET) areas. This result is listed in Table 2 and indicates that the particle size decreased with increasing DAP/Zr values. The particle size of zirconia 25DZ prepared from the sol of DAP/Zr = 0.25 was approximately one-third the value of zirconia 0DZ (DAP/Zr = 0). This corresponds to the finding that the addition of DAP effectively reduced the hydrolysis rate of ZTP and stabilized the resulting sol.

In the present study, the gels were calcined at 773 K, which was below the typical sintering temperature used for zirconia. Thus, the prepared zirconia contained grain boundaries, but nitrogen was not able to penetrate through them. This results led to a difference between the particle size calculated from the XRD data and that calculated from the BET data. The ratio of these 2 values is defined as the agglomeration degree and is shown in Table 2. The agglomeration degree of the zirconia prepared from sol 25DZ was approximately one-half the value of the zirconia prepared from sol 0DZ. However, the zirconia that was prepared from sol 50DZ showed a large agglomeration degree, suggesting that sol 50DZ was not suitable for the preparation of zirconia membranes.

Figure 5 shows the result of the nitrogen sorption measurement for the zirconia samples as a function of DAP/Zr. The area and volume of mesopores increased with increasing DAP/Zr value, and the area and volume of mesopores for zirconia 25DZ were 3 and 4 times those of zirconia 0DZ, respectively, while the micropore volume was decreased by 27% after the addition of DAP. This suggests that DAP played a role in the development of mesopores.

Figure 6 shows the size distribution of mesopores for the zirconia membranes calcined at 773 K for 1 hour. The mesopore volume of the membrane was increased and the mesopore size distribution narrowed with increasing DAP/Zr values. The average mesopore size, calculated by the desorption data, was 3.3 nm for zirconia 25DZ. However, zirconia 50DZ showed a wider mesopore distribution, even though it possessed a higher mesopore volume, as shown in Fig. 5. To



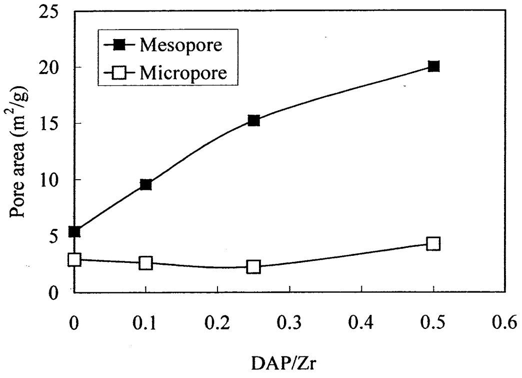


Figure 5. Effect of DAP/Zr on the volume and area of micro- and mesopores of calcined zirconia.

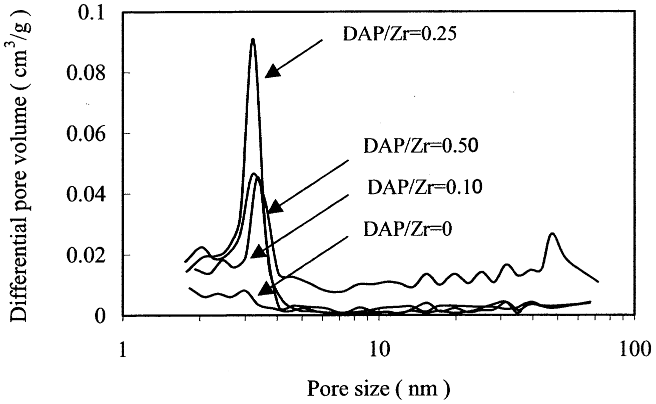


Figure 6. Effect of DAP/Zr on pore size distribution of calcined zirconia.

investigate the effect of DAP on the permeation properties of sol-gel–derived zirconia membranes, we used sols 0DZ and 25DZ to prepare the supported membranes.

Permeance Properties of Zirconia Membranes

Figure 7 shows the permeance values of the prepared zirconia membranes, suggesting that the permeation is controlled by the Knudsen diffusion mechanism.

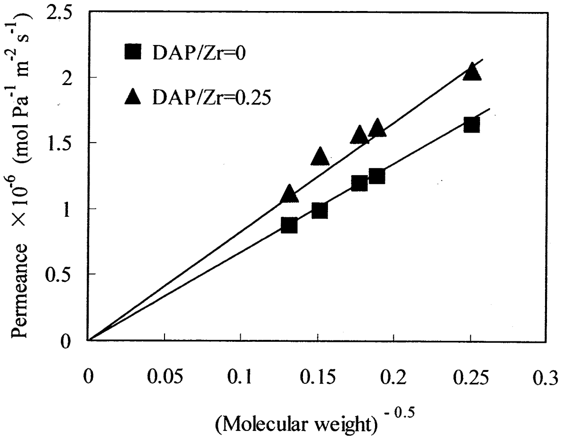


Figure 7. Permeances for zirconia membranes prepared with DAP/Zr = 0 and 0.25.

The permeance to CH_4 for membrane 25DZ was 2.05×10^{-6} mol/m^{2}Pas, which was 20% higher than that of membrane 0DZ. This result is strongly related to the pore size and volume shown in Figs. 5 and 6. Membrane 25DZ possessed a smaller average pore size and a larger porosity than did membrane 0DZ, leading to higher permeance values.

CONCLUSIONS

1. The stability of zirconia sols was greatly improved by a combination of chelation and esterification, which decreased the hydration rate by ligand exchange and by the slow release of water, respectively.
2. The zirconia membrane, which was prepared with DAP, showed a narrow pore-size distribution and a high mesopore volume. Meanwhile, the addition of DAP had almost no influence on the micropore size and decreased the phase transformation temperature.
3. The gas permeation properties of the supported zirconia membrane were fundamentally controlled by the Knudsen diffusion mechanism. The permeation properties of the membranes could be further improved and this will be the subject of a future study.

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