

Hydrolysis of ZrO₂-SiO₂ System by the Sol-Gel Method

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졸-겔법에 의한 ZrO₂-SiO₂계의 가수분해

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ABSTRACT

Monolithic gels in the ZrO₂-SiO₂ system containing up to 30 mol% ZrO₂ were prepared from the mixed solutions of Zr(O·nC₃H₇)₄ and partially prehydrolyzed Si(OC₂H₅)₄ (Tetraethyl orthosilicate) by the sol-gel method. The effect of parameters such as the hydrolysis temperature, the amount of water and HCl on the hydrolysis-condensation process was investigated and the obtained gels were studied by the IR spectra and TG-DTA. The results showed that the gelation time becomes shorter with increasing content of HCl, H₂O and gelation temperature, and that the polymerization was more easily completed with the higher water volume causing the elimination of unreacted organic groups.

요 약

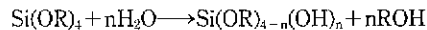
30 mol%의 ZrO₂를 함유한 ZrO₂-SiO₂계 겔을 부분 가수분해시킨 TEOS 용액과 Zr(O·nC₃H₇)₄ 용액으로부터 졸-겔법을 이용하여 제조하였으며, 졸-겔화에 영향을 미치는 반응인자인 반응온도와 물과 염산의 첨가량을 조사하였고, 얻어진 겔을 IR 및 TG-DTA 분석을 행하였다. 그 결과 겔화온도와 물과 염산의 첨가량이 증가할수록 겔화시간은 감소하였으며, 물의 첨가량이 증가하면 겔내에 존재하는 미반응 유기물의 제거로 인하여 고분자화가 거의 완료됨을 알 수 있었다.

1. Introduction

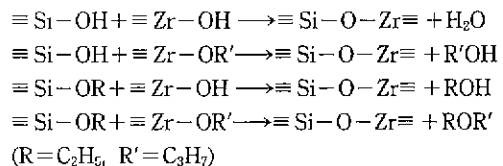
The direct conversion of gels to glass without melting has stimulated investigations in sol-gel processing¹⁻³⁾. Several reports^{4,5)} have indicated that the nature of the gel and glass formed by the hydrolysis of metal alkoxide and the degree of the overall hydrolysis may be affected by the amount of water and catalyst introduced during the preparation.

The process involves a hydrolysis reaction which is followed by condensation or polymerization. It is important to note that the polymerization has a great influence on gelation. The proposed mechanism is as follows⁴⁾:

Formula of hydrolysis



Condensation



However, sol-gel process based on the hydrolysis and condensation of alkoxides are still not fully understood and pose a number of questions which require further investigation.

In the previous report⁶⁾, it was demonstrated that the ZrO₂-SiO₂ gels were converted to pore free glass at 900°C or above and the properties such as density

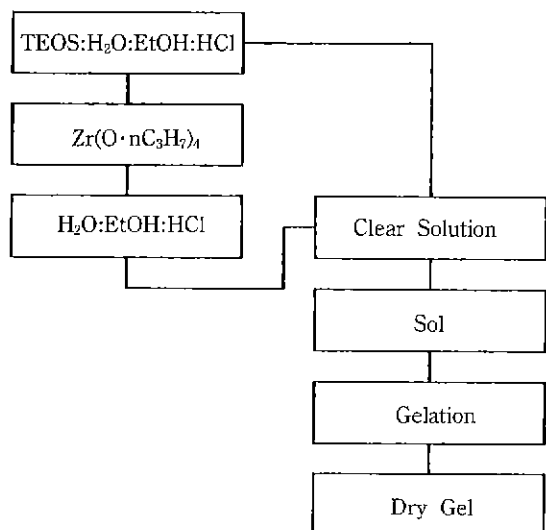


Fig. 1. The procedure for the preparation of a dry gel.

and Vicker's hardness of the glass were compared with the results of other investigators. In this paper, author discussed the effect of various processing conditions in the initial stage of the sol to gel transition of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Zr}(\text{O}\cdot\text{nC}_3\text{H}_7)_4$.

2. Experimental Procedures

2.1. Preparation of sample

Fig. 1 shows the procedure for preparing the $\text{ZrO}_2\text{-SiO}_2$ gel and silica gel. The gelation of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS, reference sample for IR spectra) was accomplished by mixing 4 mols of H_2O , 1 mol of $\text{C}_2\text{H}_5\text{OH}$ and 0.03 moles of HCl per 1 mol of $\text{Si}(\text{OC}_2\text{H}_5)_4$, the hydrolysis was carried out at 30°C . The solution had been stored in the beaker until the stiff gel formed.

The $\text{ZrO}_2\text{-SiO}_2$ system were studied at three different levels of ZrO_2 : 10, 20 and 30 mol% (designated 10Z, 20Z, 30Z) were studied. Table 1 shows the amount of materials used to prepare $\text{ZrO}_2\text{-SiO}_2$ sol. The method of the hydrolysis of metal alkoxide was similar to that developed by Yoldas⁷. TEOS was initially hydrolyzed (denoted 1st hydrolysis) with a mixed solution as listed in Table 1. $\text{Zr}(\text{O}\cdot\text{nC}_3\text{H}_7)_4$ (Fluka Co., EP grade) was allowed to react with the hydrolyzed TEOS solution at various temperature for 1 h. Then, the residual mixed solution was added (denoted 2nd hydrolysis) and stirred at the same temperature for 30 min. The clear

Table 1. The Batch Amount of Ethanol, Water and Catalyst Used in Hydrolysis

1st hydrolysis			2nd hydrolysis		
H_2O	$\text{C}_2\text{H}_5\text{OH}$	HCl	H_2O	$\text{C}_2\text{H}_5\text{OH}$	HCl
1	1	0.03	1	1	0.03
1	1	0.03	2	1	0.03
1	1	0.03	4	1	0.03
1	1	0.03	8	1	0.03
1	1	0.003	1	1	0.003
1	1	0.003	2	1	0.003
1	1	0.003	4	1	0.003
1	1	0.003	8	1	0.003

1st hydrolysis; molar ratio of TEOS.

2nd hydrolysis; molar ratio of total alkoxides.

solution was poured into a beaker and left for a few days for gelatination. The monolithic gels were heated in an electrical furnace at a rate of $10^\circ\text{C}/\text{h}$ approximately kept at 150°C for 72 h and subsequently characterized.

2.2. Gel characterization

The changes in the amount of ethanol during the partial hydrolysis of TEOS in the equimolar solutions of H_2O , ethanol and TEOS initially were monitored at various reaction temperatures using a Perkin-Elmer Gas Chromatography (GC-sigma 300) equipped with a $2\text{m}\times 1/4"$ Porapak Q column and a FID detector to be sensed at 250°C . Standard solvents (ethanol and isopropanol) were also tested. IR spectra in the range of $400\sim 2000\text{ cm}^{-1}$ were recored by the KBr pellet method using a Perkin-Elmer 1430 spectrophotometer. Thermal analysis (TG-DTA) was carried out with 20Z gels after drying at 40°C . The analysis was performed using a Rigaku PTC-10 equipment at a constant heating rate of $10^\circ\text{C}/\text{min}$ from 25°C to 900°C .

3. Results and Discussion

3.1. The effect of partial hydrolysis of TEOS at different temperature

By comparison to the standard, the peaks observed in the GC were found to be due only to ethanol. In general, the production of ethanol can be taken as a measure of the progress of the hydrolysis reaction and condensation⁸. It might be reasonable to assume that

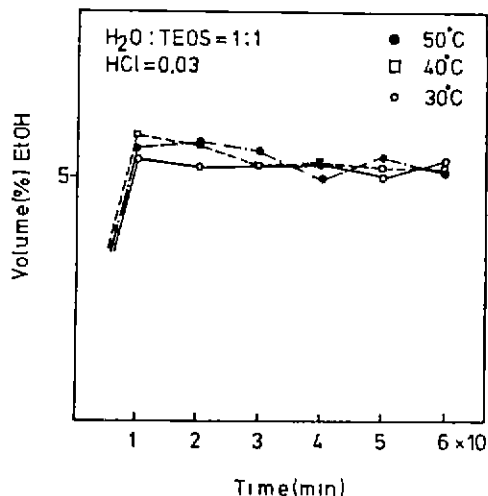


Fig. 2. The volume percentage of ethanol as a function of time with various reaction temperatures at the first hydrolysis.

the presence of ethanol should be the results of hydrolysis and condensation since no other source of the alcohol was present.

For the condition of 1:0.03:1 molar ratio of $H_2O:HCl:TEOS$, the volume percentage of ethanol vs. time at the various reaction temperatures of the partial hydrolysis of TEOS is shown in Fig. 2. The volume percentage of evolved ethanol reaches a maximum value within 10 min in all cases and then remained fairly constant with time. Although the plateau in the ethanol level varied somewhat at the various temperatures, no real significance was attributed to the variation.

It was observed that the reaction time was not temperature dependent in this experiment. It took less than 10 min for the ethanol level to reach the plateau in all cases. Apparently, the use of an acid catalyst seems to accelerate the reaction of hydrolysis and condensation⁹.

3.2. Gelation time at various condition

$TEOS$ and $Zr(O\cdot nC_3H_7)_4$ were polymerized in the presence of water and a catalyst by hydrolysis and subsequent polycondensation. The solution forms gel in a few minutes to tens of hours. The gelation time was dependent on the amount of water, HCl and gelation temperatures, as shown Fig. 3. Sufficient water ($R: H_2O/TEOS \geq 4$) and higher gelation temperature seem to accelerate the gelation of sols. We also found that

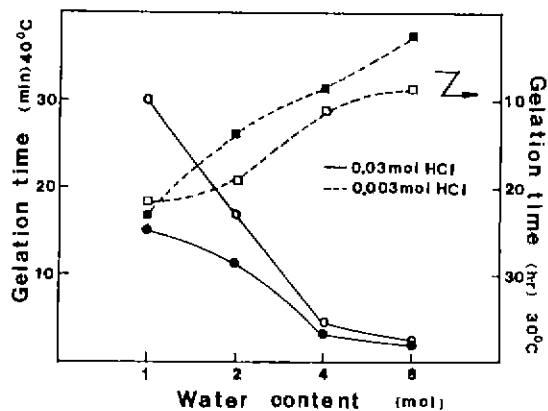


Fig. 3. The gelation time with content of water, HCl at gelation temperatures of 30 and 40°C, (opened: 30°C, closed: 40°C).

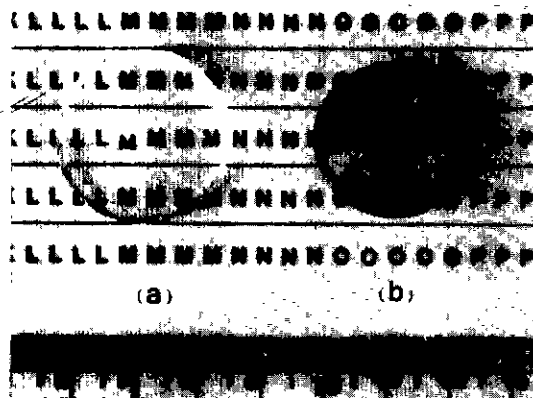


Fig. 4. The photograph of a 20Z gel.
a) Dry gel at 40°C b) Dry gel at 150°C

the gelation time was proportional to the HCl concentration with equal water content, resulting in the value of the minimum gelation time for the higher HCl concentration¹⁰.

Monolithic gels were obtained from all sols except one prepared with less water. They shrunk to one fourth of the initial volume after drying for two weeks. The appearance of the gels are shown in Fig. 4.

3.3. IR spectra

Fig. 5 shows the IR spectra of silica gel and 20Z gels with various water content. In the silica gel the spectra shows four absorption bands at around 1085 (with a shoulder at 1200 cm^{-1}), 800 and 465 cm^{-1} (which are characteristics of silica oxides). The first

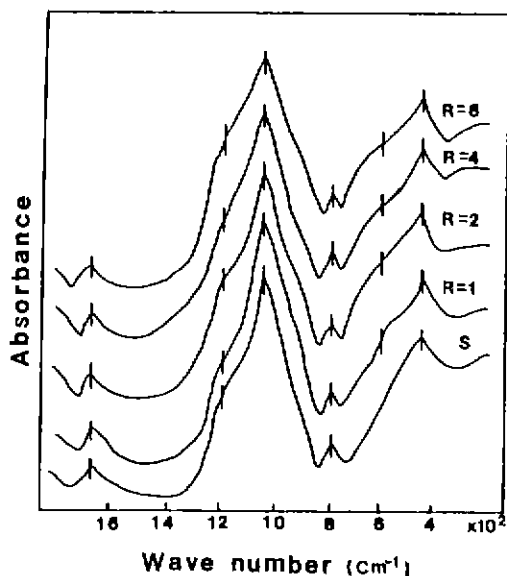


Fig. 5. The IR spectra of a 20Z gels with various water content after heating at 150°C. (S: silica gel)

two bands correspond to asymmetric and symmetric Si-O stretching motions and the last one to a bending Si-O-Si mode¹¹. The band at 1600 cm⁻¹ is assigned to the deformation vibration of the H-O-H bond of water which is adsorbed on the gel or KBr powder¹¹.

A comparative study of the IR spectra of the gel obtained by TEOS polymerization and with those of the gels from the polymerization of TEOS with Zr(O-nC₃H₇)₄ may help understand of the change of the structure of a gel. The new absorption band at 600 cm⁻¹ is found in the 20Z gel in addition to the absorption bands due to Si-O bonds with the peaks around 1600, 1085, 800 and 460 cm⁻¹. The former is attributed to Zr-O bond⁹, and the absorption band at 600 cm⁻¹ might be associated with the ZrO₈ groups in which the Zr⁴⁺ does not enter into the total anionic framework structure of the gel: Zr⁴⁺ ion takes up a position in the interstices of the network structure of ZrO₂ groups. The intensity of the band increases as H₂O content increases.

IR spectra, however, do not give enough information on the degree of polymerization, since the bands corresponding to the organic or hydroxyl groups of alkoxides are either too broad to permit interpretation or overlapping with the bands of Si-O vibration¹².

A more suitable method of determining the degree

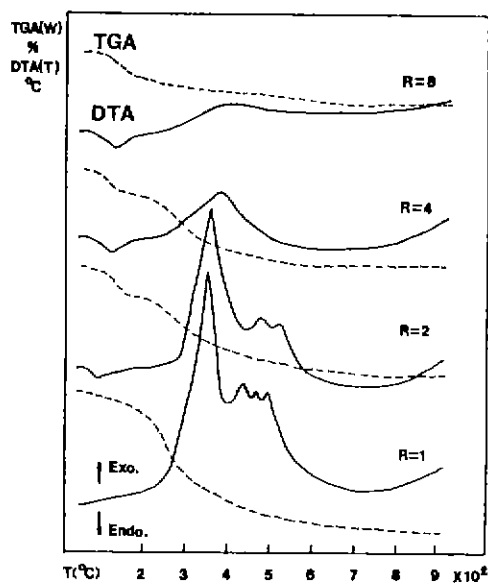


Fig. 6. The thermogram for 20Z gels at various water contents.

of polymerization as a function of the residual organic groups may be the DTA and TGA study of the gel decomposition.

3.4. TG-DTA measurements

Fig. 6 shows TG-DTA curves of 20Z gel with various water contents as a function of temperature. In the gel with R=1, no endothermic peak appears around 80°C indicating an incomplete hydrolysis process with a lack of free water. Instead, a strong and sharp exothermic peak appear at 350°C, probably due to the decomposition of the remaining organic groups.

IR does not detect unreacted organic groups in the gel. The carbonization of organic residues occupied in the gel appears from 420°C to 540°C as three exothermic peaks. In the gel with R=2, an endothermic peak at 80°C appears due to the loss of 3.6% of water and alcohol. Observed exothermic peak in the result of pyrolysis of the organic residues in the gel at 360°C, but two exothermic peaks by the carbonization appear between 450°C and 560°C. The TGA curves show that the number of total organic group is less in the R=2 gel than in the R=1 gel.

In the gel with R=4, TG-DTA curve shows an endothermic peak at 80°C appears due to the loss of 4.2% of water and alcohol. Hydrolysis and polymerization

seem to be more complete because of the greater amount of water.

In the gel with $R=8$, an endothermic peak appears at $85^\circ C$ due to the loss of 4.9% of water and alcohol. The remaining peaks disappeared, indicating total polymerization and less unreacted organic groups left. The last results show that the polymerization becomes more complete with higher water volume, causing the organic groups to react more completely and the number of organic residual peaks to decrease. Also, the total percent weight losses decrease with increasing R , as a result of the increasing overall hydrolysis and consequent removal of alkyl groups.

4. Conclusions

The formation of gels containing ZrO_2 up to 30 mol% in ZrO_2 - SiO_2 system through hydrolysis and condensation of metal alkoxide was examined by measurement of gelation time under various conditions, IR spectra and TG-DTA of the gels with various water content.

The conclusion can be summarized as follows:

1) The minima in partial hydrolysis time of TEOS are independent of the hydrolysis temperature. The hydrolysis rate of mixed solution is rapidly reacted by the increase of HCl, H_2O content and reaction temperature.

2) The gelation time of the solution hydrolyzed by 0.03 moles of HCl and 8 moles of H_2O is about 100 times shorter than that of the solution hydrolyzed with 0.003 moles of HCl and 1 mol of H_2O content.

3) IR spectra of 20Z gel show that the Zr^{4+} ion is incorporated in the interstices of the silica network structure.

4) In the TG-DTA, the polymerization is more com-

plete with higher water volume causing the organic groups to react more completely and the number of organic residual groups to decrease.

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