

CHAPTER IV RESULTS AND DISCUSSION



4.1 Gel Characteristics

This section demonstrated the effect of preparation variables, viz. pH and molar water to precursor ratio (R_H), on gel characteristics and gel time.

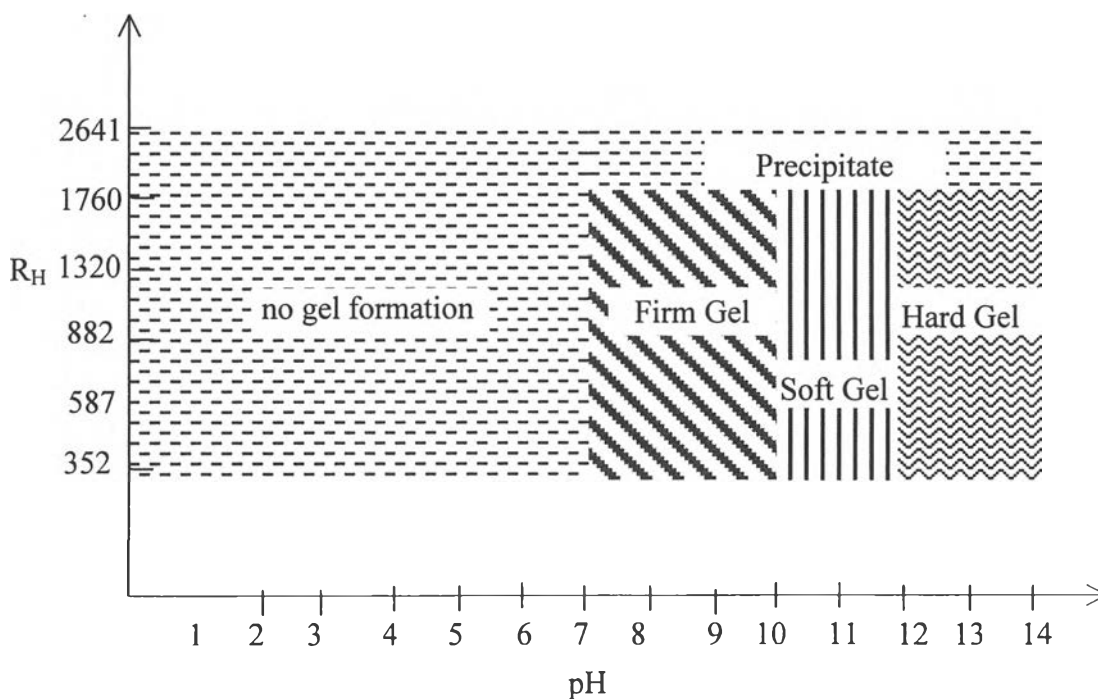


Figure 4.1 Effect of pH and the molar water to precursor ratio (R_H) on the gel formation.

4.1.1 Gel Zone

Important preparation variables and the appearance of the resulting gel products are summarized in Figure 4.1. The effect of pH on the characteristics of gel was studied by adjusting the pH with oxalic acid and NH_4OH at constant R_H values ranging from 352 to 2641.

For all R_H values of 352-1760, gel occurred with the same pattern along the pH value, as shown in Figure 4.1. When a greater amount of oxalic acid was used (at the pH value below 7), no gelation occurred, indicating that the cross-linking decreased with lowering pH. The excess amount of acid strongly inhibited

the condensation process, resulting in no gel formation. With the pH of 7-10, a firm gel was formed immediately. These gels were in milky white color. When no acid was used, at the pH of 10-12, the gel was completely soft and clears. With the pH of 12-14 (adjusted by NH_4OH), the hard gel was formed.

At the pH 7-14, when the R_H reached 2641 and beyond, white precipitates were formed immediately, without going through the gelation, as illustrated on the top of the gel zones.

4.1.2 Gel Time

Gel time is one of those factors demonstrating the rates of hydrolysis and condensation. The shorter gel time indicates the higher hydrolysis and condensation rates.

At the R_H of 587, the optimum result giving the best surface area and pore volume, this condition was thus selected to study the effect of pH on the gel time. In addition, at the R_H of 1320 was also selected to study the effect of pH on the gel time in order to confirm the result. A gel was formed at different pHs adjusted by adding oxalic acid or NH_4OH . The change in gel time with pH is shown in Figure 4.2. With the pH of 7 to 10, a white gel was formed immediately. At pH 11-12, the gel time increased to 3 hours, while pH 13-14, it took 2 hours to obtain gel.

The precursor is in the form of basic substance whose aqueous solution has the pH around 11-12. Therefore, gel can be formed at pH 11-12 without adjusting with the acid or base. The gel time at pH 11-12 was about 3 hours. On the other hand, to prepare a gel at pH 7-10, an amount of oxalic was needed. The acid stimulated the hydrolysis rate, which also caused the condensation rate increased sequentially, leading to the shorter gelation time. On the other hand, for the case when gel was formed at pH 13-14, NH_4OH added to adjust the pH might have stimulated the condensation rate, but not as much as the acid might have. Therefore, the gel time at pH 13-14 was longer than those at pH 7-10 and shorter than those at pH 11-12.

In conclusion, adjusting pH affected the hydrolysis and condensation rates in the sol-gel process.

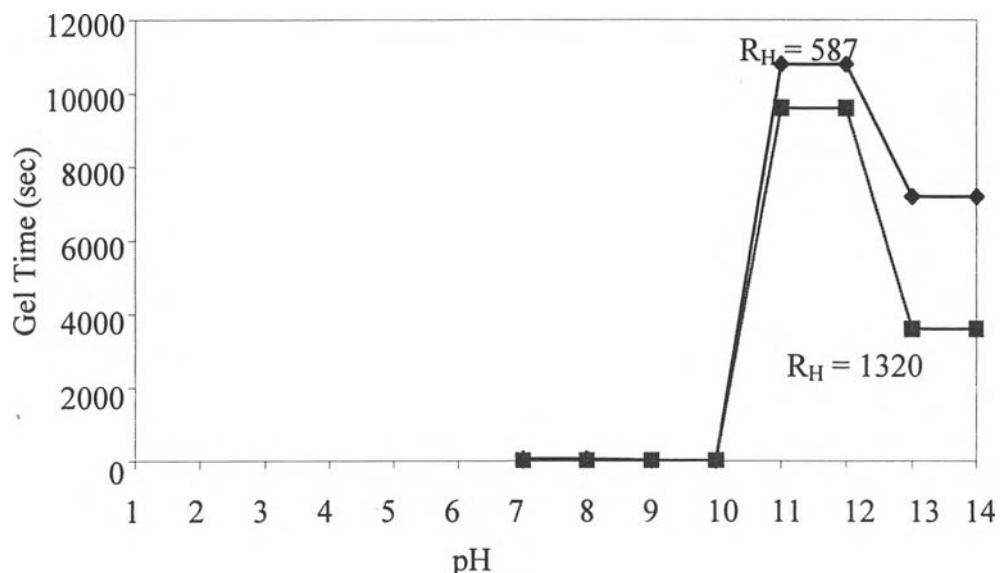


Figure 4.2 Effect of pH on gel time obtained at the R_H of 587 and 1320.

The amount of water in the sol-gel process representing in the term of R_H also affected the gel time. When the water ratio was increased from 352 to 1760 at pH of 11-12 and pH 13-14, the gel time decreased (Figure 4.3). From the result, it can be seen that the increase in water available for hydrolysis increased hydrolysis rate and the number of M-OH groups. The increase in concentration of M-OH groups increased the condensation reaction, and consequently decreased the gel time.

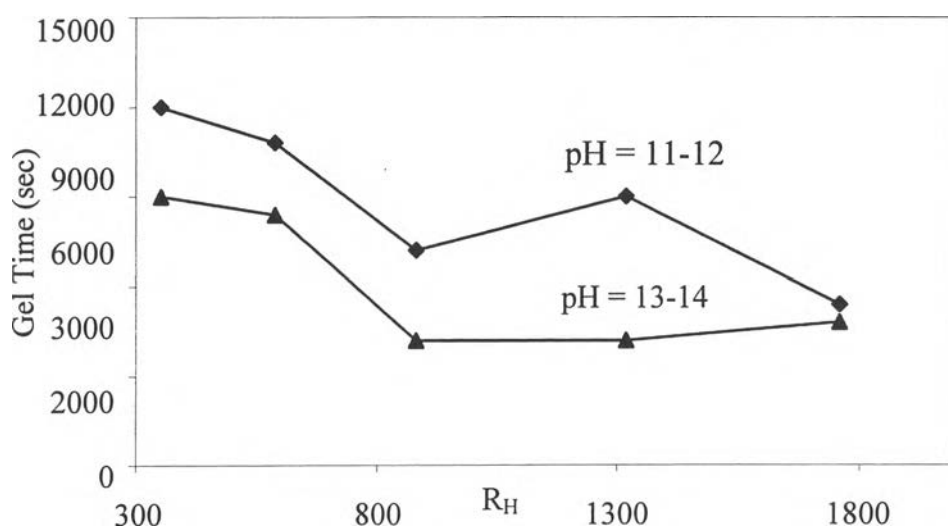


Figure 4.3 Effect of the R_H on gel time at pH 11-12 and 13-14.

4.2 Catalyst Characterization

4.2.1 Sodium Content

Since the precursor used in this research was in the form of sodium compound, which could affect to the catalyst activity, it was required to remove sodium in the oxide preparation. Therefore, to reduce the sodium content in zirconia, gel washing is essential for removing the amount of sodium from zirconia to ensure high purity. The gel samples prepared at pH 11-12 with the R_H of 587 were washed with different numbers of washing times. AAS analysis was carried out on the oxide samples calcined at 600°C in order to determine their sodium content. Figure 4.4 shows that the sodium content decreases with increasing the number of washing times. However, the weight loss of zirconia increased when the number of washing times increased. From AAS results, it could be concluded that 3 time washing was optimal due to the sufficiently low amounts of sodium, and no significant change with more washing times.

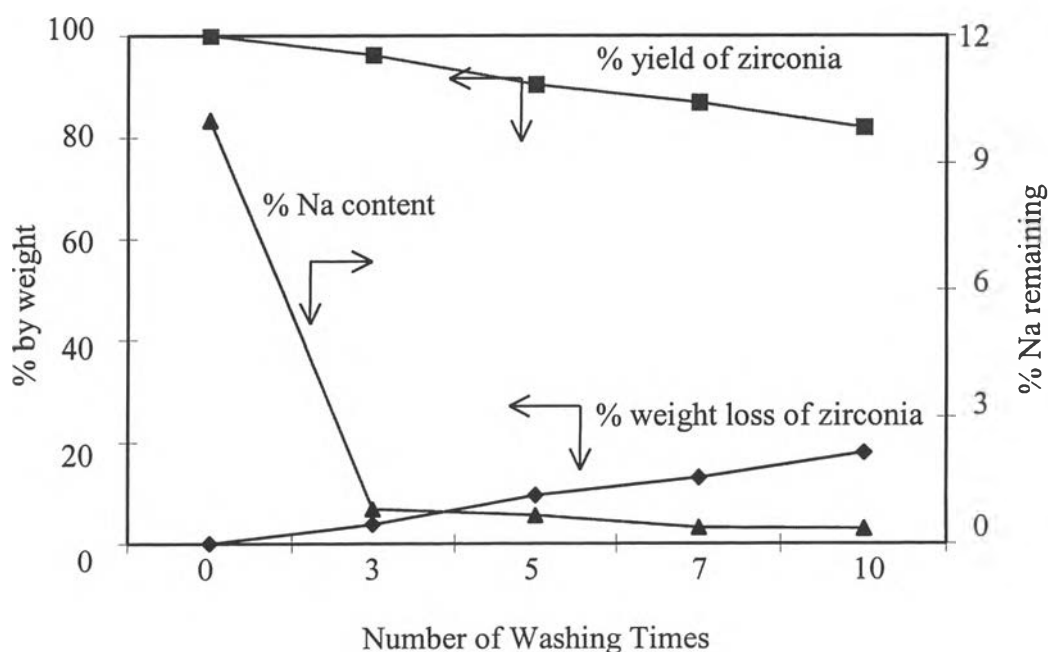


Figure 4.4 Sodium removal from gel formed from the R_H of 587 at pH 9-10.

4.2.2 Phase Transfer

To study the effect of heat treatment on the crystal structure of zirconia, a gel was formed at pH 11-12 and R_H of 587. X-ray diffraction was employed for crystal structure determination. As shown in Figures 4.5 and 4.6, zirconia is amorphous with heat treatment of 400°C and below. After calcination at higher temperatures, the modification of the solid structure took place. When the calcination temperature increased, the peaks of the X-ray diffraction, especially at 30°, 35° and 50° (2θ) significantly sharpened, indicating that the amorphous zirconia became the tetragonal phase after calcination at 500°C, as observed from the normal curve of tetragonal phase of zirconia in Appendix C2. Additionally, X-ray diffraction data showed that heating to 700 ° C caused the zirconia to transform into the monoclinic phase. As shown in Figure 4.6, the monoclinic zirconia oxide showed the three main reflections typical peak of zirconia (at around the 2θ of 25°, 28° and 32°).

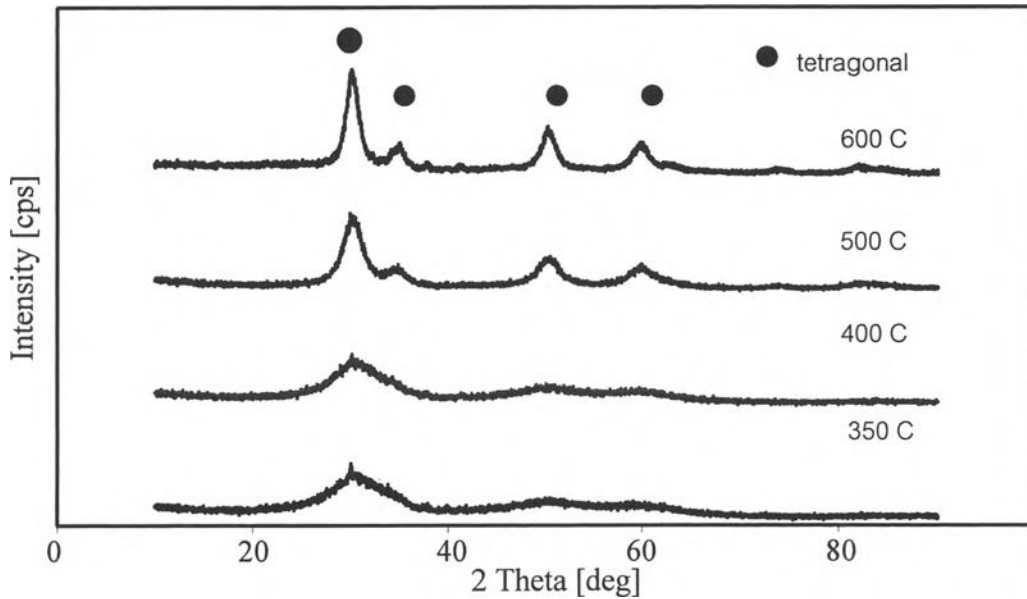


Figure 4.5 Influence of calcination temperature on phase composition of zirconia prepared with the R_H of 587 at pH 9-10 during gelation step.

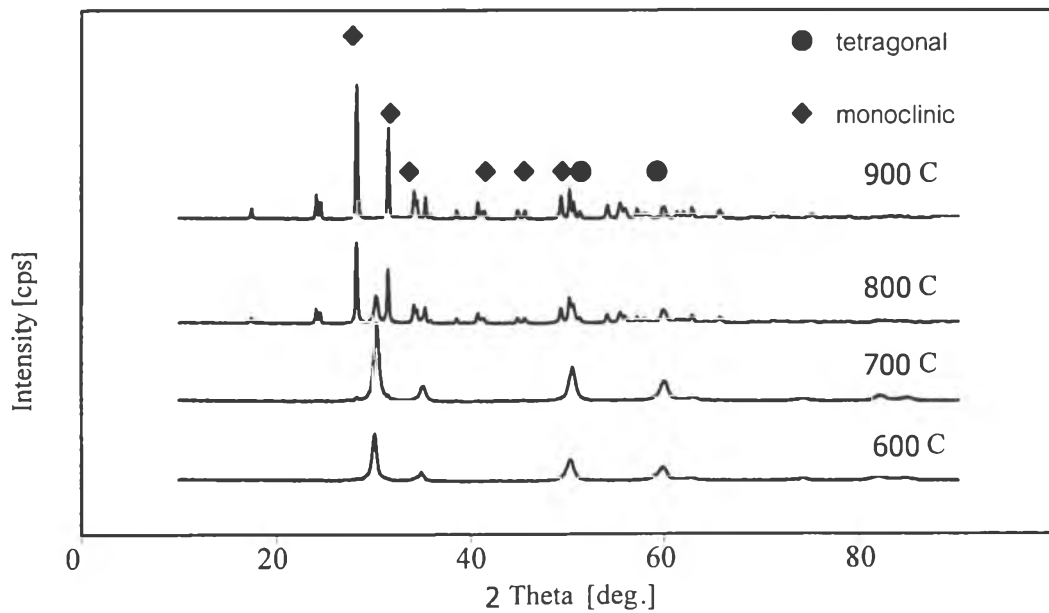


Figure 4.6 Influence of calcination temperature on phase composition of zirconia prepared with the R_H of 587 at pH 9-10 during gelation step.

4.2.3 Weight Loss

TGA technique was employed to measure the weight loss as increasing temperature. Figure 4.7 illustrates the TGA and DTA profiles of zirconia prepared with the R_H of 587 at pH 11-12 and calcined at 600°C. The first peak of the weight loss observed up to 110°C is due to the removal of physically absorbed water on zirconia. The second peak observed between 700° to 800°C is due to the transformation of tetragonal to monoclinic phase of zirconia, as also confirmed by XRD. According to XRD results described previously, the phase transfer occurred at 700°C or more.

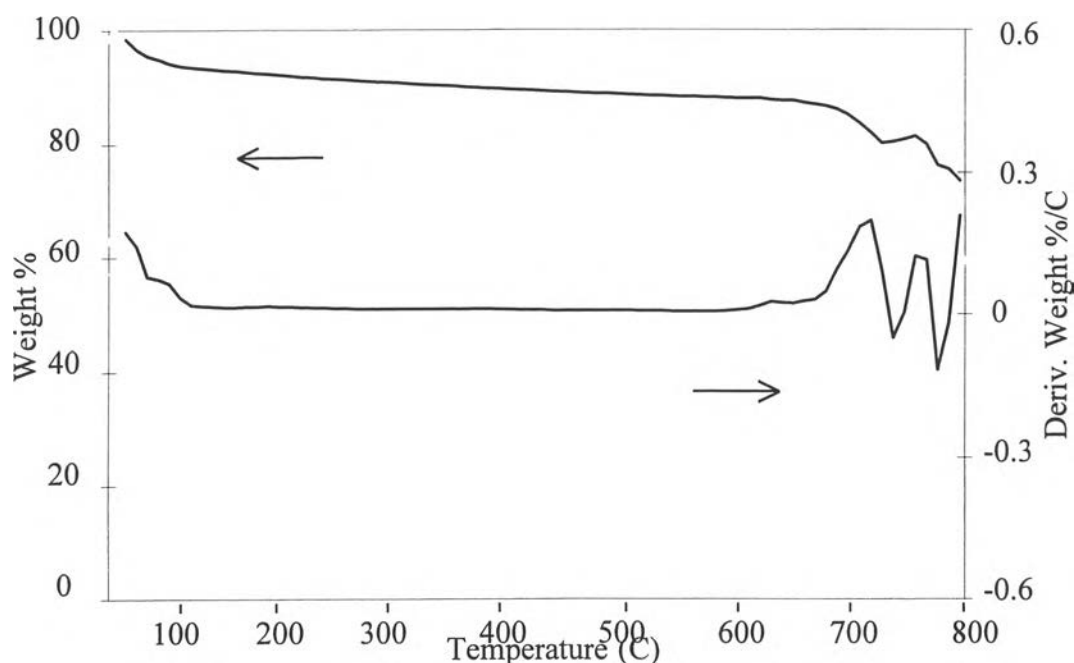


Figure 4.7 TGA and DTA curves of zirconia prepared with the R_H of 587 at pH 11-12, and conducted at 10 K.min⁻¹ with the air flowrate of 25 ml/min.

4.2.4 Morphology

The effect of the pH on the gelation is important to the textural and size of the solid oxide particle. The shape of the particles is illustrated in Figure 4.8. The ZrO₂ particles are too small to be distinguished at 10,000 magnification. A comparison between micrographs with the same magnification indicated that large particles were obtained in the case of pH 7- 8 and 9-10, and smaller particles were

observed when the oxides were prepared at pH 11-12 and 13-14. It was observed that the gels formed with longer gel time yielded smaller particles of oxides with higher surface area.

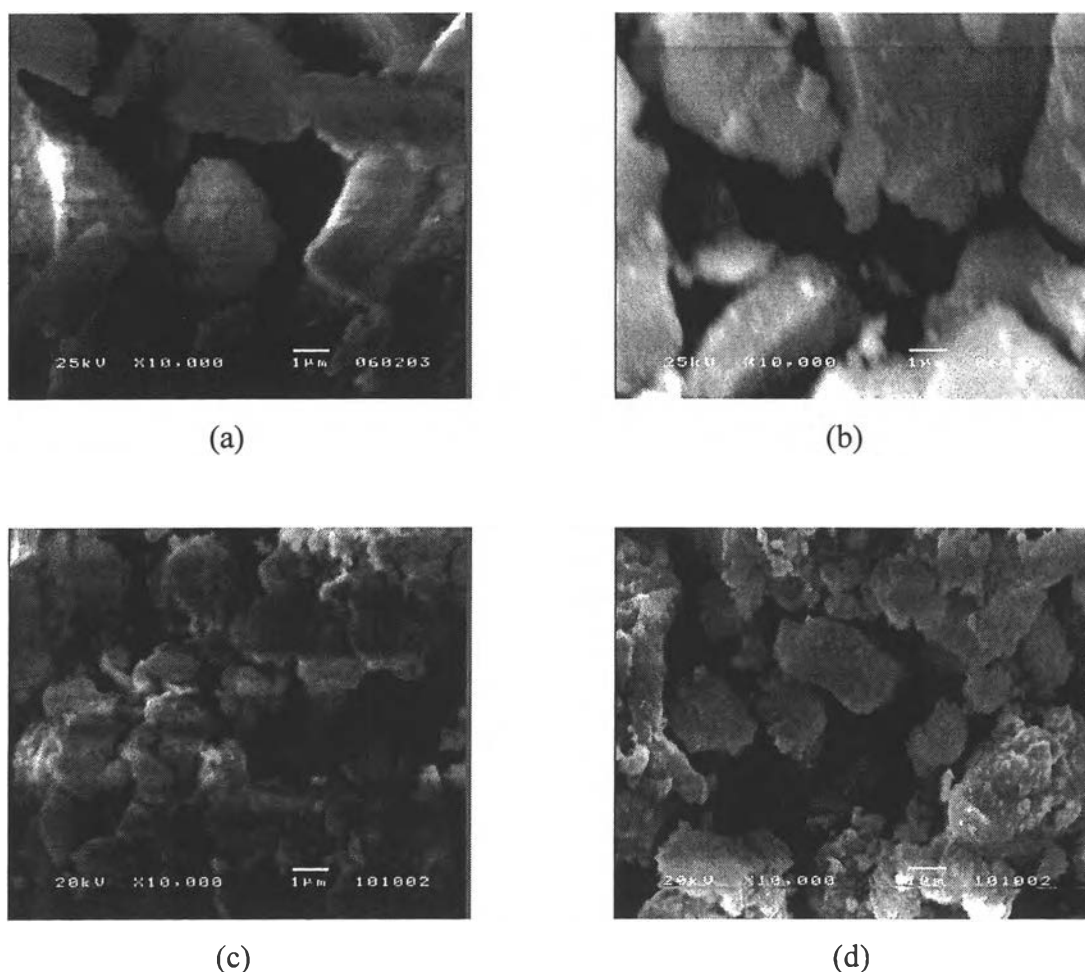


Figure 4.8 SEM pictures of zirconia prepared with the R_H of 587 at: (a) pH 7-8, (b) pH 9-10, (c) pH 11-12, and (d) pH 13-14, and calcined at 600 °C.

4.2.5 Physical Properties

To study the effect of pH and the R_H on the physical properties of zirconia, an Autosorb-1 gas sorption system was used to obtain nitrogen adsorption/desorption isotherms. Before analysis, all samples were out-gassed for 3 hours under vacuum at 250°C. From the 22-point adsorption and desorption isotherm, BET surface area, S_{BET} , the specific pore volume, $V_p(N_2)$, the pore size

diameter, d_p , and the pore size distribution of the zirconia calcined at 600°C were calculated.

4.2.5.1 Adsorption Isotherm

Zirconia samples were characterized by N_2 adsorption. Figure 4.9 shows the adsorption isotherms for the zirconia obtained with the R_H of 587 at pH 11-12. The adsorption isotherms for other zirconia samples prepared with different conditions are similar. These isotherms exhibit broad hysteresis loops, which are characteristic of adsorbents possessing a high proportion of mesopores.

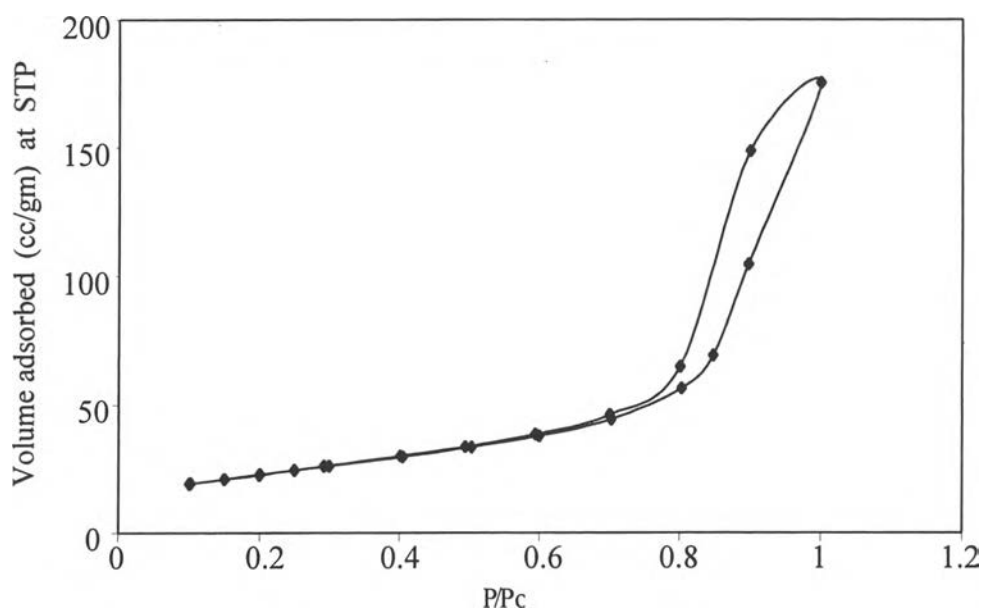


Figure 4.9 Typical adsorption/desorption isotherms of nitrogen physisorption on zirconia prepared with the R_H of 587 at pH 11-12.

4.2.5.2 BET Surface Area

Upon the variation of R_H , the BET surface areas, S_{BET} , of the zirconia calcined at 600°C varied in a small range for all pHs, as illustrated in Figure 4.10. In contrast, the surface area of oxide highly depends on pH in the gel formation step. By optimizing the water and pH condition, zirconia formed at the pH 11-12 with the R_H of 587 gave the highest surface area of ca. $125\text{ m}^2/\text{g}$ after calcination at 600°C for 4.5 hours, whereas S_{BET} was only ca. $19\text{ m}^2\cdot\text{g}^{-1}$ for the samples prepared at pH 8 with the R_H of 882. Figure 4.11 shows the maximum surface area obtained at pH 11-12 with a constant R_H of 587, the change in BET surface area with different pH condition follows the following order:

$$\text{ZrO}_2(\text{pH 11-12}) > \text{ZrO}_2(\text{pH 9-10}) = \text{ZrO}_2(\text{pH 13-14}) > \text{ZrO}_2(\text{pH 7-8}).$$

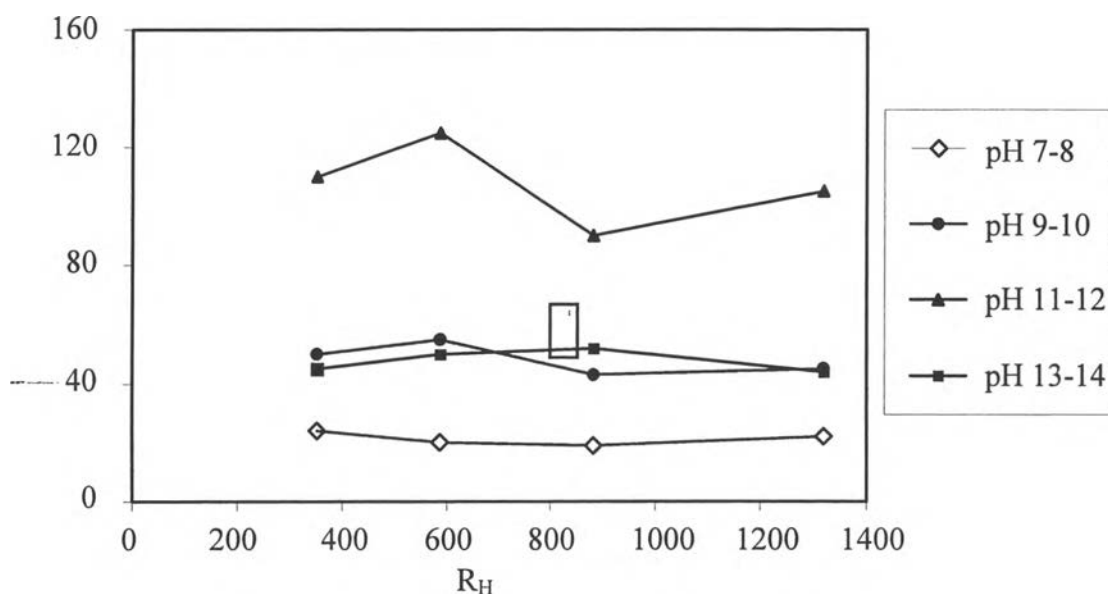


Figure 4.10 BET surface area of ZrO_2 , after calcination at 600°C for 4.5 hours, as a function of the R_H and pH.

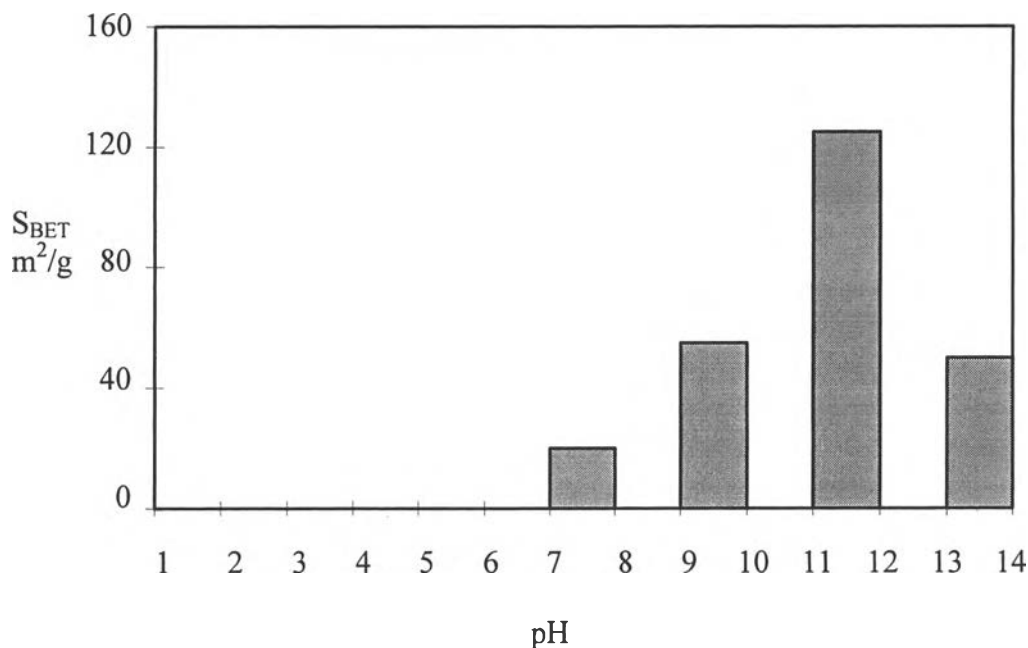


Figure 4.11 BET surface area of ZrO_2 , prepared with the R_{H} of 587, and calcined at 600°C for 4.5 hours, as a function of pH.

4.2.5.3 Pore Volume

The pore volumes of these zirconias were also investigated. According to Figures 4.12 and 4.13, the maximum pore volume of $0.077 \text{ cm}^3/\text{g}$ is obtained for zirconia prepared at pH 11-12 with the R_{H} of 587. With these conditions, longer time was required to form gel, leading to a more cross-linked network, and resulting in a decrease in the average pore size, and increase in its specific surface area and pore volume. The specific pore volume of zirconias increased in the following order:

$$\text{ZrO}_2(\text{pH } 11-12) > \text{ZrO}_2(\text{pH } 9-10) = \text{ZrO}_2(\text{pH } 13-14) > \text{ZrO}_2(\text{pH } 7-8)$$

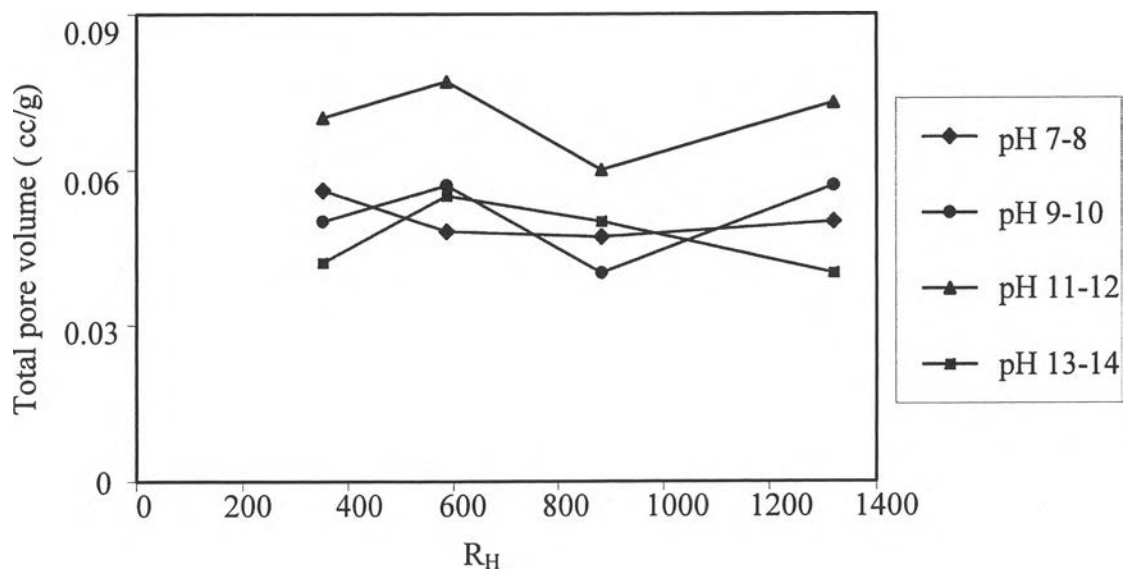


Figure 4.12 Total pore volume of ZrO₂, after calcination at 600°C for 4.5 hours, as a function of the R_H and pH.

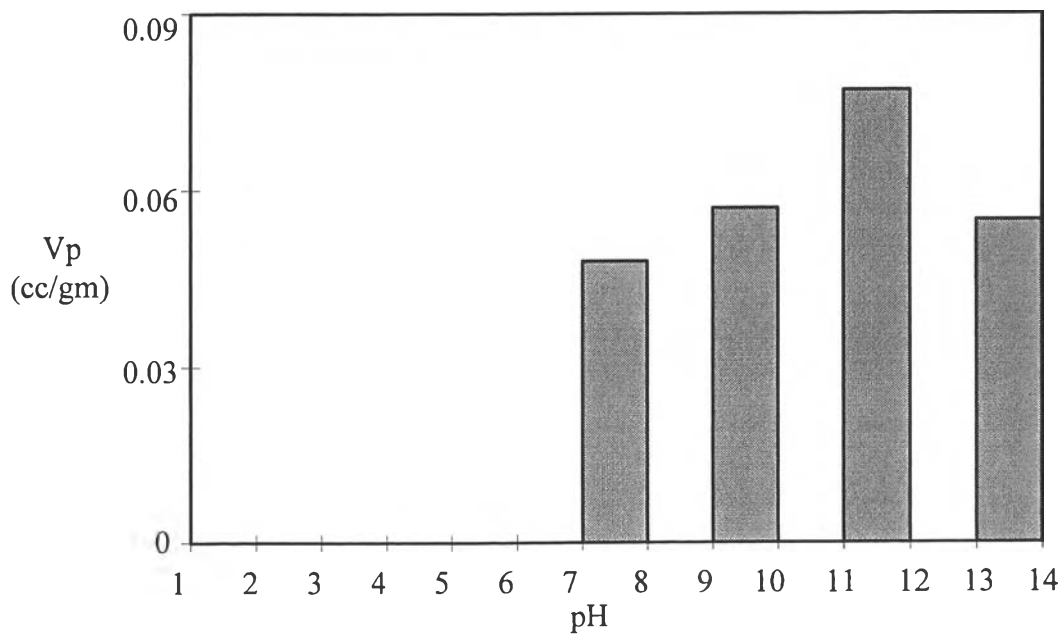


Figure 4.13 Total pore volume of ZrO₂, prepared with the R_H of 587, and calcined at 600°C for 4.5 hours, as a function of pH.

4.2.5.4 Pore Size

For pore size, all prepared sol-gel zirconia had pore radius between 30 to 96 Angstroms. Figures 4.14 and 4.15 shows that the lowest pore size diameter was obtained when zirconia was prepared with the R_H of 587 at pH 11-12. The pore size of zirconia in the following order:

$$\text{ZrO}_2(\text{pH 11-12}) > \text{ZrO}_2(\text{pH 9-10}) = \text{ZrO}_2(\text{pH 13-14}) > \text{ZrO}_2(\text{pH 7-8})$$

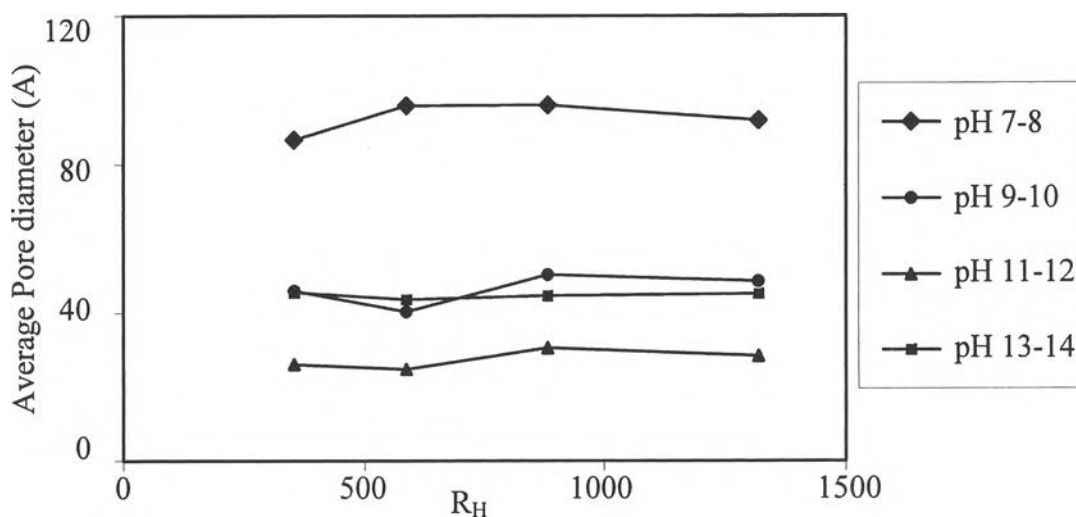


Figure 4.14 Average pore diameter of ZrO_2 , after calcination at 600°C for 4.5 hours, as a function of R_H and pH.

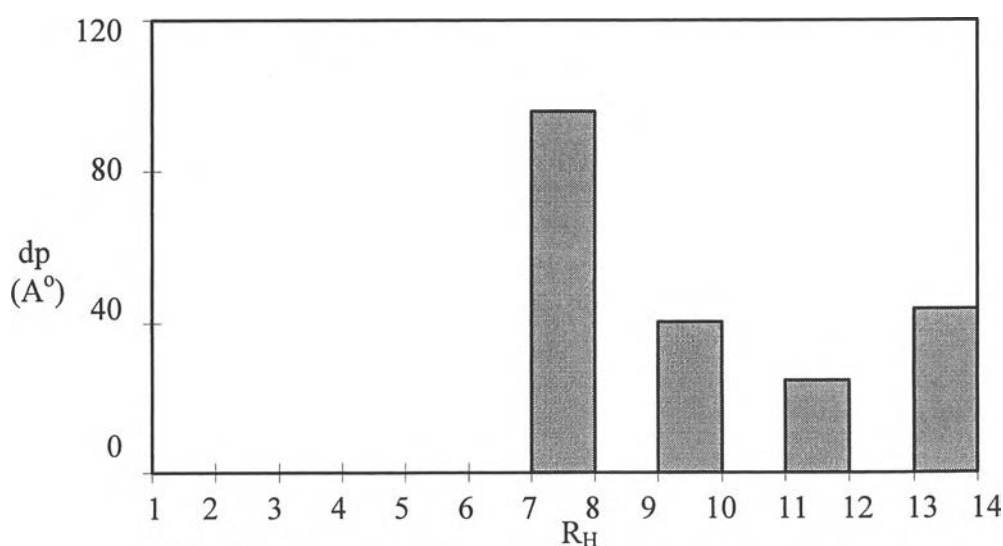


Figure 4.15 Average pore diameter of ZrO_2 , prepared with the R_H of 587, and calcined at 600°C for 4.5 hours, as a function of pH.

4.2.5.5 Pore Size Distribution

Figures 4.16 (a), (b), (c), and (d) show the pore size distributions of zirconia prepared with different pHs and a constant R_H of 587, calcined at 600°C. Most of them showed unimodal pore size distribution. The pH condition caused the distribution to change. The sample prepared at pH of 7-8 had a pore size distribution center around 100 Angstrom. Increasing the pH condition resulted in a shift of the dominant pore size maximum from larger to smaller number. Zirconias prepared at pH 9-10 and 13-14 had a pore size distribution center around 50 Angstrom, whereas zirconia prepared at the pH of 11-12 had a bimodal pore size distribution, as shown in Figure 4.16 (c). The Figure shows a group of small pore radii centered around 30°A and a group of macropores at about 90°A.

From the physical property data, it can be seen that the optimal condition was at pH 11-12, which could be explained in terms of gel time. The slower gel time, the more network was the created. The more network increased the higher surface area and the pore volume as well. In contrast, at pH 7-10, the gel time duration was short, providing less time for particles to grow, as a result, creating less network structure. The oxide product had thus very little surface area and pore volume.

The variation of pH in the sol-gel process showed a strongly effect on the physical properties of zirconia whereas the influence of R_H has little significant effect.

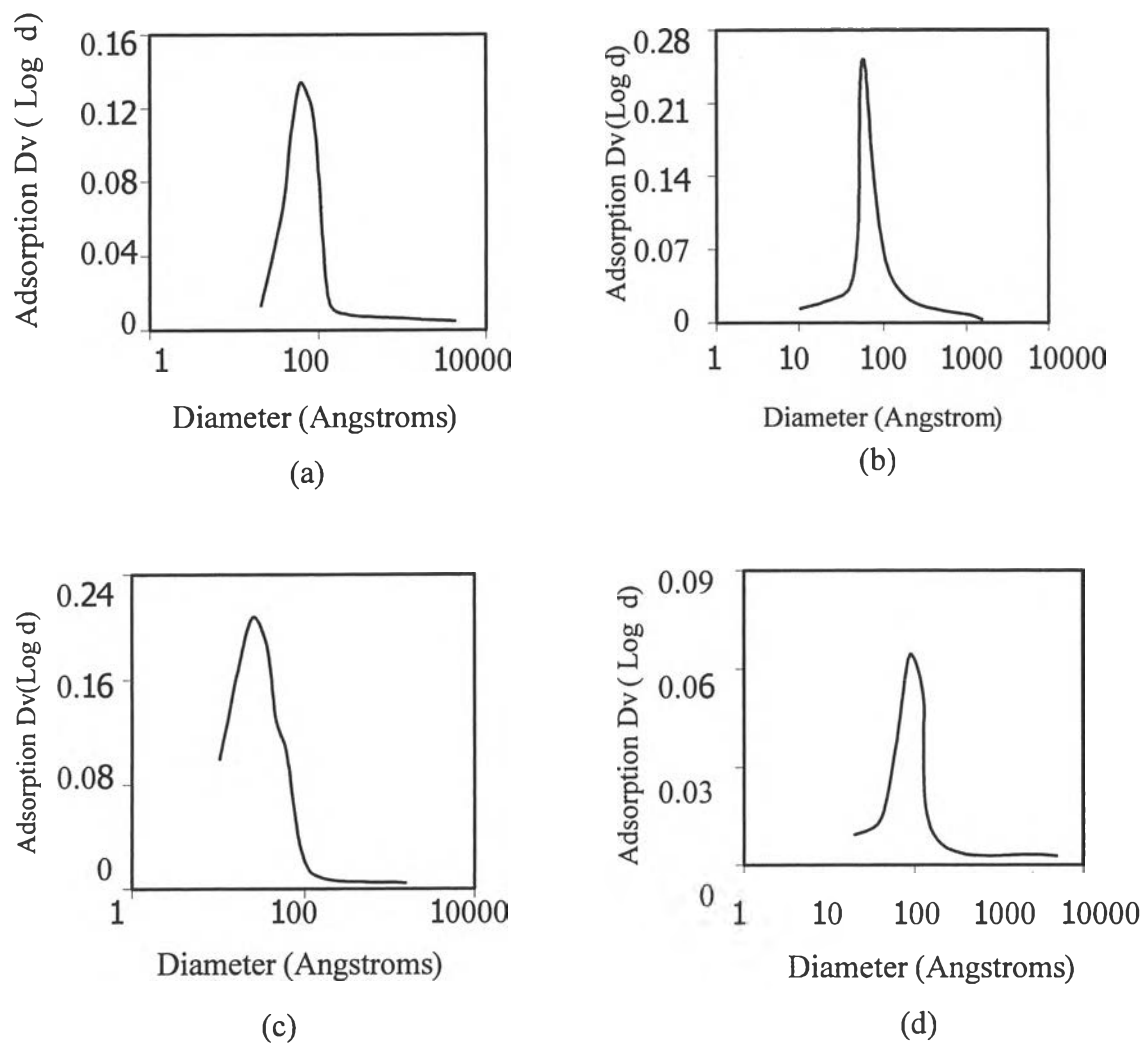


Figure 4.16 Pore size distribution of zirconia prepared with the R_H of 587 and calcined at 600 °C: (a) pH 7-8, (b) pH-10, (c) pH 11-12, and (d) pH 13-14.

4.2.6 Acidity & Basicity

Temperature programmed desorption measurements of NH_3 and CO_2 were conducted to examine the acidity and basicity, respectively, on the zirconia prepared at different pHs. Figure 4.17 shows a TPD of NH_3 for the zirconia catalysts. Ammonia desorbs through a wide temperature, resulting in a broad peak with a maximum desorption occurring at around 120°C . Zirconia formed at pH 11-12 gave the typical dual – peak TPD signals at 150 (peak1) and 250°C (peak2), whereas the others were observed with one broad peak at around 100°C . Acidity of the oxides were determined by integrating the TPD curves. Over the range of the pH condition, zirconia prepared at pH 11-12 had the highest acidity. The change in acidity by pH condition is in the following order:

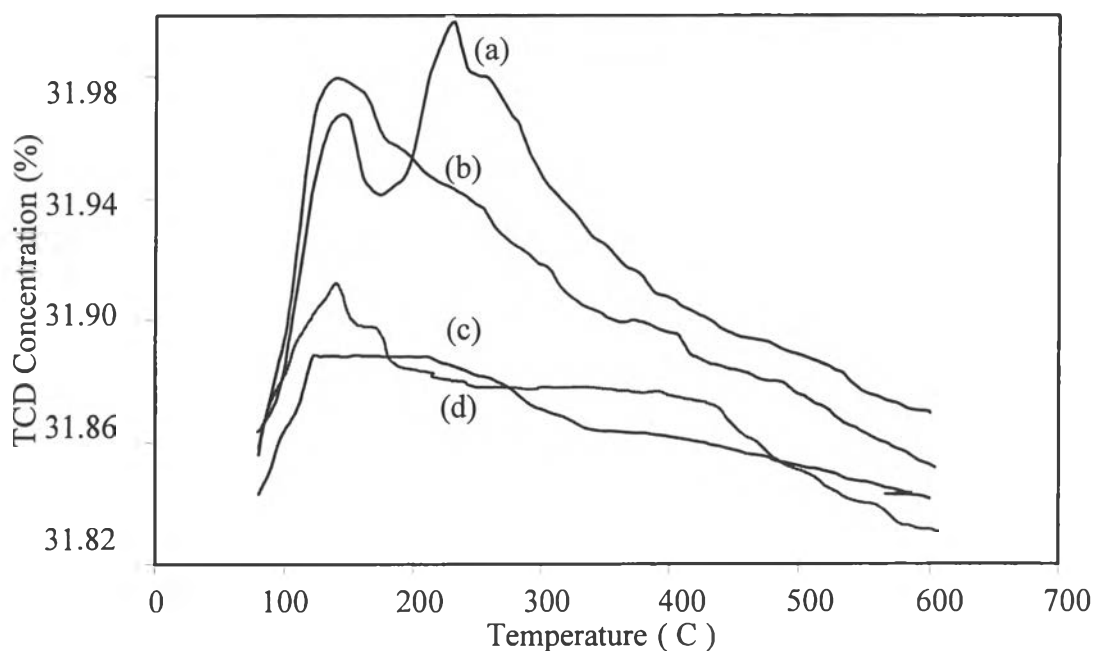
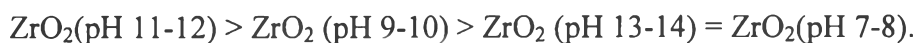


Figure 4.17 Acidity of zirconia using temperature-programmed desorption of NH_3 at $5^\circ\text{C}/\text{min}$ and pH: (a) 11-12, (b) 9-10, (c) 7-8, and (d) 13-14.

The TPD profiles of CO₂ desorption on zirconia oxides are shown in Figure 4.18. With the pH of 11-12, the desorption of the solid started at 70°C, producing a peak with a maximum approximately at 150°C. In the case of pH 13-14, these two broad peaks appear at about 100° and 200°C, whereas in the case of pH 9-10 and 7-8 small desorption peak was shifted to lower temperature around 90°C. The change in basicity by pH condition in the following order:

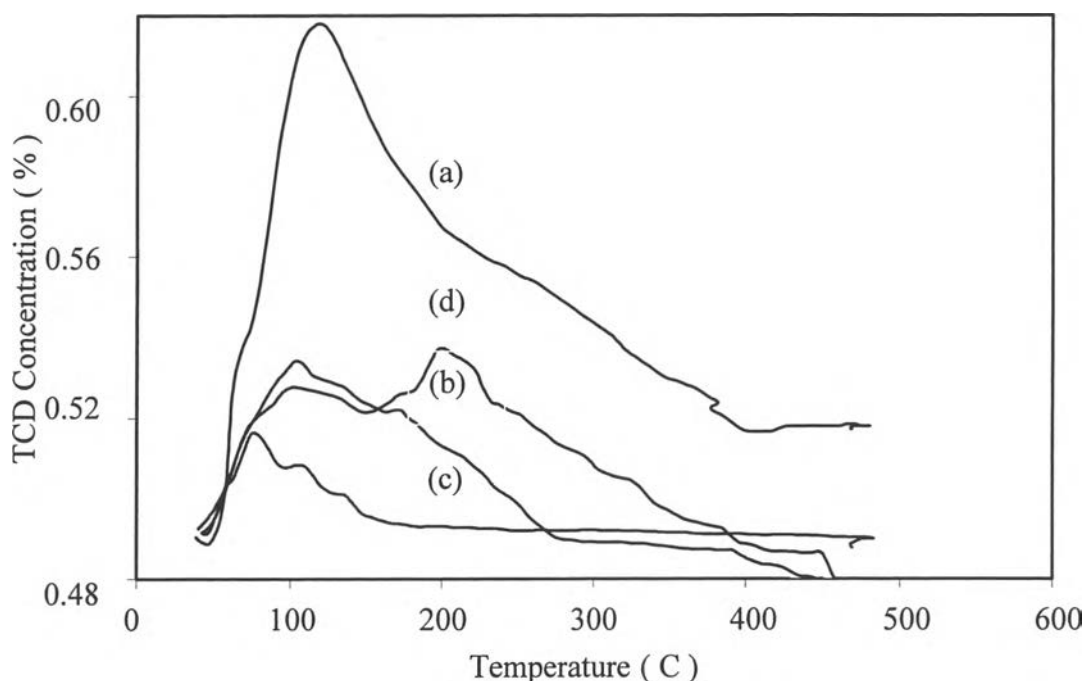
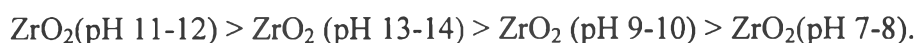


Figure 4.18 Basicity of zirconia using temperature-programmed desorption of CO₂, at 5 °C /min and pH: (a) 11-12, (b) 9-10, (c) 7-8, and (d) 13-14.

The surface of zirconia shows both acidic and basic behaviors, which are the characteristics of an amphoteric oxide. The surface structure of zirconia is shown in Figure 4.19. There are three important sites on zirconia: Bronsted acid, Bronsted base, and Lewis acid, as generated from the reactions listed under Figure 4.19. The mechanism on the acidic surface may occur by a proton transfer from a Bronsted acid site to an adsorbed molecule or by an electron pair transfer of from an adsorbed molecule to a lewis acid site, thus forming an acidic addition product. In

addition, the mechanism on basic surface can occur by the transfer of an electron pair from Bronsted base site to the adsorbed species.

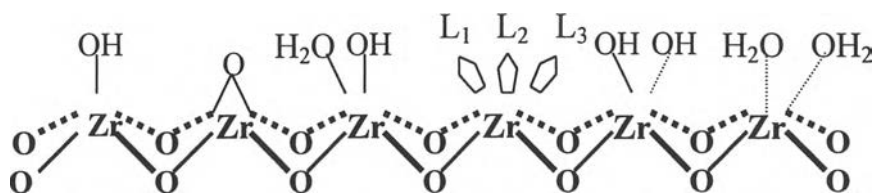
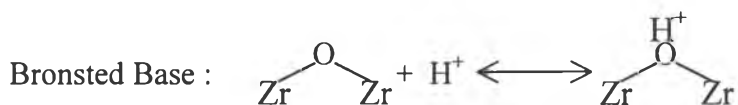
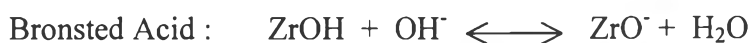


Figure 4.19 Nature of Zirconia Surface (Zhang *et al.*, 1999).



The analysis of TPD of NH_3 and CO_2 can be seen that the oxide with high acidity also has high basicity because of its largest gel network formed from the largest gel time, resulting in the highest surface area. So, there was a large number of acidic and basic sites on the surface of oxide formed from large network gel. In other words, the proton from Bronsted acid is easy to protonate onto NH_3 molecule. The status of the electron on the surface was changed and tended to transfer to the next molecule of zirconia. Then, the zirconia surface became higher acidic and basic. However, at pH 13-14, the oxide had high basicity but low acidity. Under basic condition, gel time duration was so long that it caused highly branched networks of gel and a large number of oxygen-bridge or Bronsted base site on the surface.