CHAPTER IV
RESULTS AND DISCUSSION

4.1 Precursor Synthesis and Characterization

Cerium glycolate complex was synthesized by Oxide-One-Pot-Synthesis process (OOPS). The reaction of cerium hydroxide, ethylene glycol, and sodium hydroxide was obtained by heating the reaction mixture in a magnetically stirred, standard pyrex distillation setup and slowly distilling off the ethylene glycol under nitrogen at atmospheric pressure to immediately remove by-product and water from the reaction. Triethylenetetramine (TETA) was employed as a catalyst with small amount of sodium hydroxide as co-catalyst to achieve the desired product. In both reactions, ethylene glycol served not only as a solvent but also as a reactant, forming two bidentate chelates for cerium hydroxides. This was the reason why an excess ethylene glycol, disstilled off with removal of water, was essential to achieve the high percentage yields of the products. The product provided powder at approximately 90% isolated yield. The product was isolated by addition of dried acetonitrile to result in yellow-green solids of cerium glycolate complexes.

Repeated washing with dried acetonitrile was necessary to remove residual triethylenetetramine and ethylene glycol. According to above investigation, cerium glycolate complexes were thus prepared as illustrated in Figure 4.1
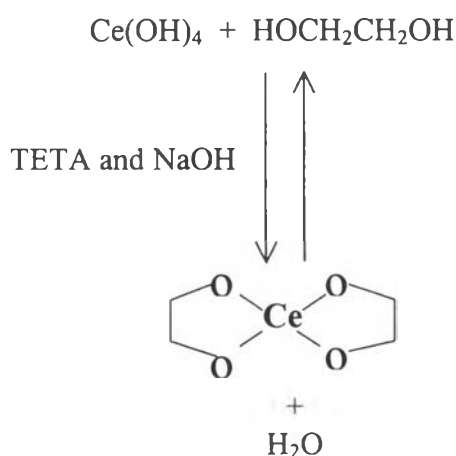
$$Ce(OH)_4 + HOCH_2CH_2OH$$

TETA and NaOH

$$+$$

$$H_2O$$

Figure 4.1 Cerium glycolate complex.

FTIR, ^{1}H-NMR, TGA, and mass spectrometer were used to investigate the structure of cerium glycolate complex product.

The FTIR spectra of the product shown in Figures 4.2 compares with its corresponding starting materials with similar bands at around 3700-3000 cm^{-1} and a band at 1600 cm^{-1}, corresponding the v(O-H) stretching and bending vibrations of absorbed water by the products, respectively. The bands located at 2939 and 2873 cm^{-1} are assigned to the v(C-H) stretching frequencies. The C-H deformation vibrations are attributed to the bands in the region of 1400-1200 cm^{-1} of methylene groups. As for cerium glycolate complex, the resonance at 1080 cm^{-1} is ascribed to the Ce-O-C stretching vibration, and the band at 550 cm^{-1} is, posible, resulted from the Ce-O stretching frequency.
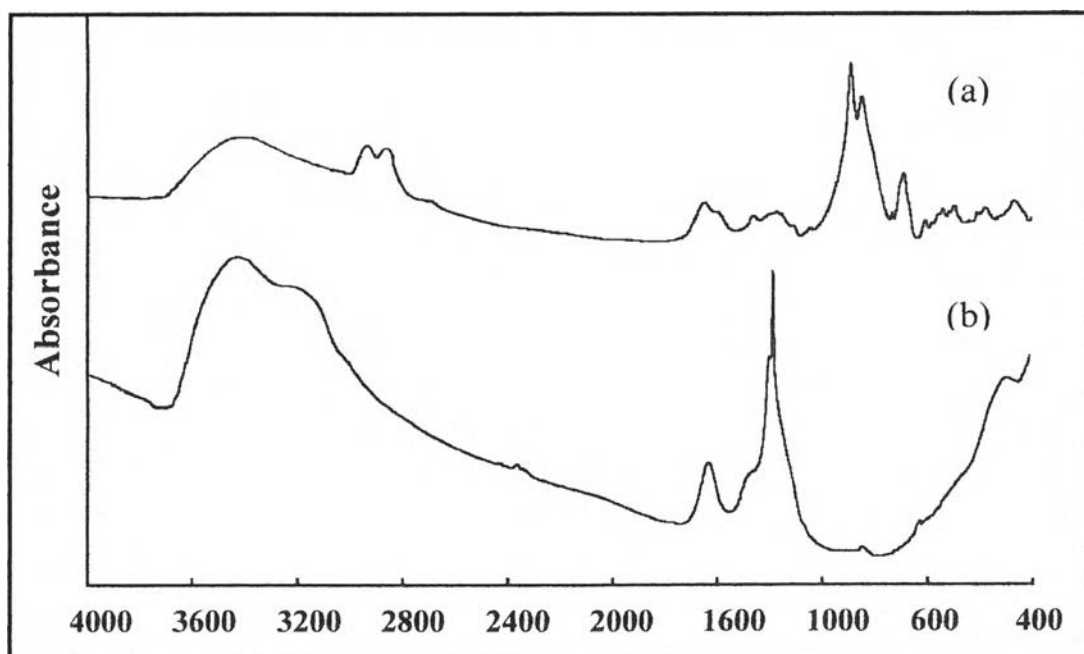

Figure 4.2 The FTIR spectra of (a) Cerium glycolate complex, and (b) CeOH₄

The ^{1}H-NMR spectra of product recorded in deuterated DMSO is shown in Figures 4.3. It can be seen that ^{1}H-NMR spectra attributed to the as-synthesized product shows only one singlet peak at 3.4 ppm. assigned to chelated glycolate ligands of CH_2-O-Ce.
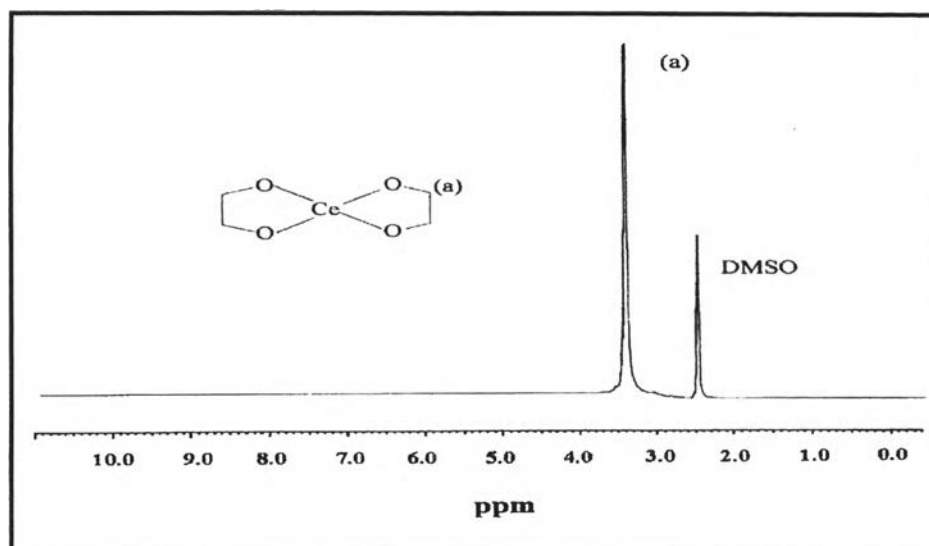
Figure 4.3 The ^{1}H-NMR spectra of Cerium glycolate complex.
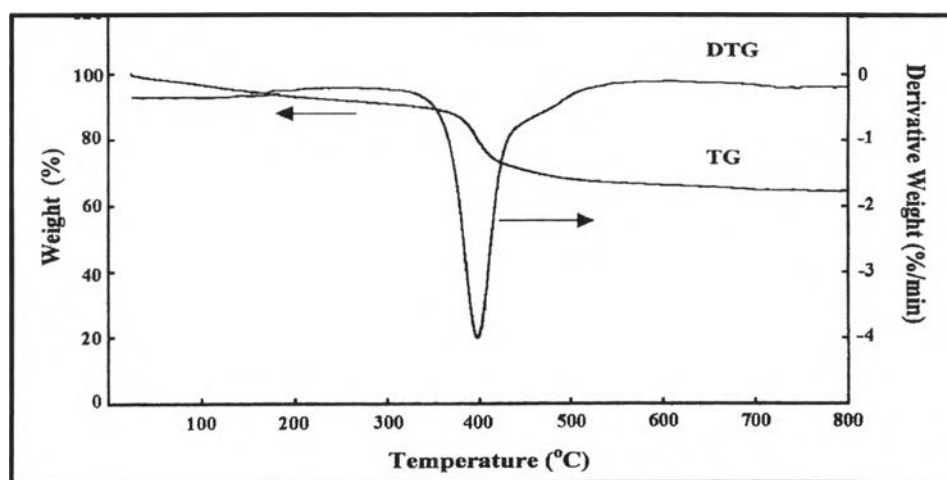

Figure 4.4 The TGA of Cerium glycolate complex.

The TGA result of cerium glycolate complex as illustrated in Figure 4.4 shows one transition at around 350-525°C. It is attributed to the weight loss of the total breakdown of organic species, resulting in the metal oxide CeO_2. The product gave the percentage ceramic yield of 65.9, which was in agreement with the theoretical yield (66.1%).

4.2 Sol-Gel Process

4.2.1 Effect of Sol-Gel Parameters.

4.2.1.1 Effect of acid ratio

In order to determine the effect of sol-gel parameters on the formation and properties of ceria gel, a series of gels were formed with different acid and water contents at room temperature. First parameter examined was the effect of acid molar ratio on crystallinity, morphology, gel time, and surface area of cerium dioxide. At a constant water to cerium glycolate complex with the molar ratio of 50, the gels were formed with using different amounts of hydrochloric acid as shown in Table 4.1. The change in gel time with acid amount are listed in Table 4.1. When the HCl : alkoxide molar ratios of less than 0.8 were used, alkoxide cannot completely dissolve in the solutions. When a greater amount of acid was used, a clear yellow solution occurred, and after that solid gel was formed. A larger acid amounts beyond this point drastically increased the gel time. When the larger HCl : alkoxide molar ratios than 1.2 were used, clear yellow solutions occurred, and after that, yellow precipitates formed.

The above series of gels were heated to 773 K, which was a common catalyst pretreatment temperature. Their BET surface area are also shown in Table 4.1. The maximum surface area of 148 m^2/g occurred at the HCl : alkoxide molar ratio of 0.8. More or less acid decreased the surface area.

Table 4.1 Gel time at different preparation conditions, and surface area of CeO_2 determined after calcination at 773 K for 1 hour.

Acid : alkoxide (mole : mole)	Water : alkoxide (mole : mole)	Gel time (s)	Surface area (m^2/g)
0	50	0-not soluble	62
0.1	50	0-not soluble	Not available
0.2	50	0-not soluble	Not available
0.3	50	0-not soluble	68
0.4	50	0-not soluble	70
0.5	50	0-not soluble	73
0.6	50	0-not soluble	75
0.7	50	Suddenly became gel	79

(Cont.)

Table 4.1 (Continued) Gel time at different preparation conditions, and surface area of CeO_2 determined after calcination at 773 K for 1 hour.

Acid : alkoxide (mole : mole)	Water : alkoxide (mole : mole)	Gel time (s)	Surface area (m^2/g)
0.8	50	868	148
0.9	50	931	139
1.0	50	1183	124
1.1	50	5206	106
1.2	50	Precipitated	85
1.3	50	Precipitated	80
1.4	50	Precipitated	71
1.5	50	Precipitated	68
1.6	50	Precipitated	60
1.7	50	Precipitated	Not available
1.8	50	Precipitated	Not available
1.9	50	Precipitated	Not available
2.0	50	Precipitated	50
0.8	20	Precipitated	Not available
0.8	40	Precipitated	Not available
0.8	50	868	148
0.8	55	208	156
0.8	60	774	152
0.8	65	1494	118
0.8	100	Sol	65
0.8	120	Sol	Not available

Even though the actual sol-gel chemistry is complex, qualitatively it can be thought in terms of the following two steps :

Hydrolysis :

$$M(OR)_n + xH_2O \longleftrightarrow M(OR)_{n-x}(OH)_x + xROH \qquad (1)$$

Condensation :

$$M\text{-}OH + HO\text{-}M \longleftrightarrow M\text{-}O\text{-}M + H_2O \qquad (2)$$

$$M\text{-}OR + HO\text{-}M \longleftrightarrow M\text{-}O\text{-}M + ROH \qquad (3)$$

During the hydrolysis step, a nucleophilic substitution occurs when the negative partial charge of the oxygen in water attacks the electropositive metal atom.

A proton shift from the water to an -OR group creates an alcohol leaving group. The condensation step also consists of a nucleophilic substitution. The oxygen electrons of an M-OH group attack the metal atom of either an M-OH or M-OR group. Again, a proton shift creates a leaving group of either ROH or H_2O. Thus, an M-O-M bridge is formed.

The addition of hydrochloric acid did not only speed up the hydrolysis rate by protonating the -OR ligand, providing a better leaving group, but also increase the gel time by decreasing the rate of condensation. The decrease in surface area was due to increasing amount of acid. Furthermore, the gelation time also affects the organization of the molecule, as can be seen in pore size distribution results. The lower acid amount provides less time to arrange itself, thus, molecule forming less uniform as already mentioned above. From Table 4.1, gel obtained from the highest acid amount results in the lowest. gelation time. As the gel time lengthened further the condensation reaction were slowed down so much. The large particles formed with little bridging between them upon heating. This network contained large particles with less open space and hence the surface area and pore volume decreased. Moreover, the images from SEM (Figure 4.5) suggest a collapsed ceria structure.

4.2.1.2 Effect of water ratio

The effects of water ratio were examined by performing a similar set of experiments. When the H_2O : alkoxide molar ratio increased while maintaining a constant HCl : alkoxide molar ratio, the alkoxide concentration was reduced. This in turn reduced the hydrolysis and condensation rate, resulting in longer gel time. Another reason was that water, which was the by-product of the condensation reaction causing a larger value of H_2O : alkoxide molar ratio, reversed condensation reaction. At constant acid amount, decreasing the water content increased the gel time. The case at constant water ratio, the gel time behavior with respect to acid content was identical, those with larger acid contents increase the gel time. The decrease in water available for hydrolysis reduced the number of M-OH groups present. This decrease in concentration of M-OH groups slowed down the condensation reaction, increaseing the gel time. The surface area results for both water ratios are shown in Table 4.1.
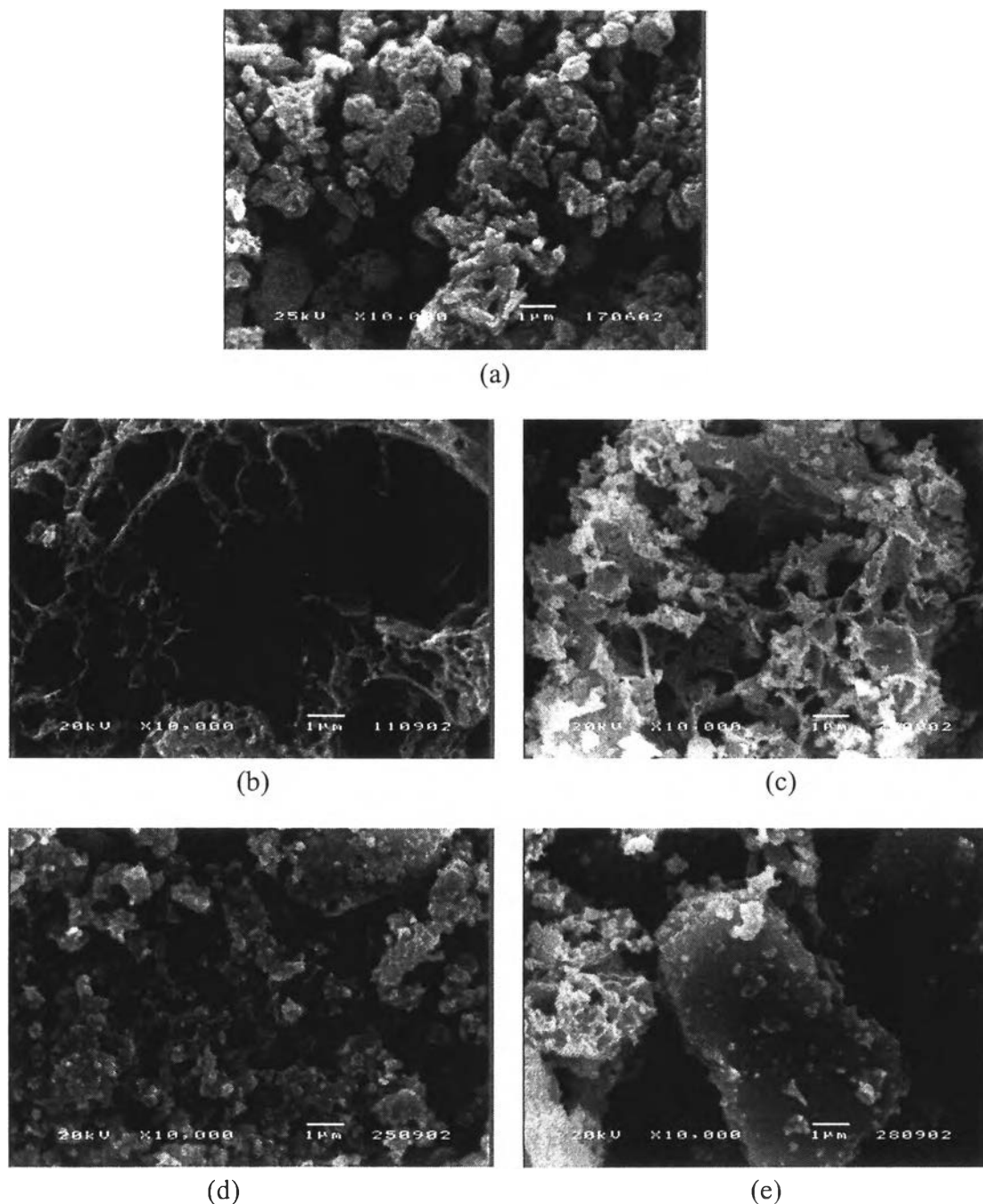
(a)

(b)

(c)

(d)

(e)

Figure 4.5. Secondary Electron Images of CeO_2 prepared with different acid : alkoxide molar ratios at fixed water : alkoxide molar ratio of 50 and calcined at 673 K for 1 hour. (a) acid : alkoxide = 0:1, (b) acid : alkoxide = 0.8:1, (c) acid : alkoxide = 0.9:1, (d) acid : alkoxide = 1:1, and (e) acid : alkoxide = 1.1:1.

4.2.1.3 Effect of heat treatment

To study the effect of heat treatment on ceria oxide, the experiments were performed on a sample prepared with the HCl : alkoxide : water molar ratio of

0.8 : 1 :55. This formulation exhibited the highest surface area in the initial screening. Nitrogen adsorption/desorption performed after each heat treatment step were used to show the effect of heat treatment on the pore structure of cerium dioxide. With the calcination temperature at 633 K for 1 hour, the highest surface area was achieved. The surface area results from these experiment are shown in Table 4.2. The collapse of surface area and pore volume did occur with heat treatment, as indicated by SEM (Figure 4.6).

With optimized sol-gel parameters, which are amount of acid, amount of water, and amount of alkoxide. CeO_2 consistently formed with the surface area of 156 m^2/g. The highest observed surface area was 180 m^2/g which achieved from the lowest temperature for and the shortest time for calcination.

Table 4.2 Surface area of CeO_2 at varied temperatures and calcination times.

Temperature (K)	Time (hr.)	Surface area (m^2/g)
673	1	180
673	3	155
673	5	137
673	7	121
773	1	156
773	3	133
773	5	117
773	7	105
873	1	100
873	3	81
873	5	67
873	7	55
973	1	80
973	3	62
973	5	53
973	7	47
1073	1	71
1073	3	58
1073	5	50
1073	7	45
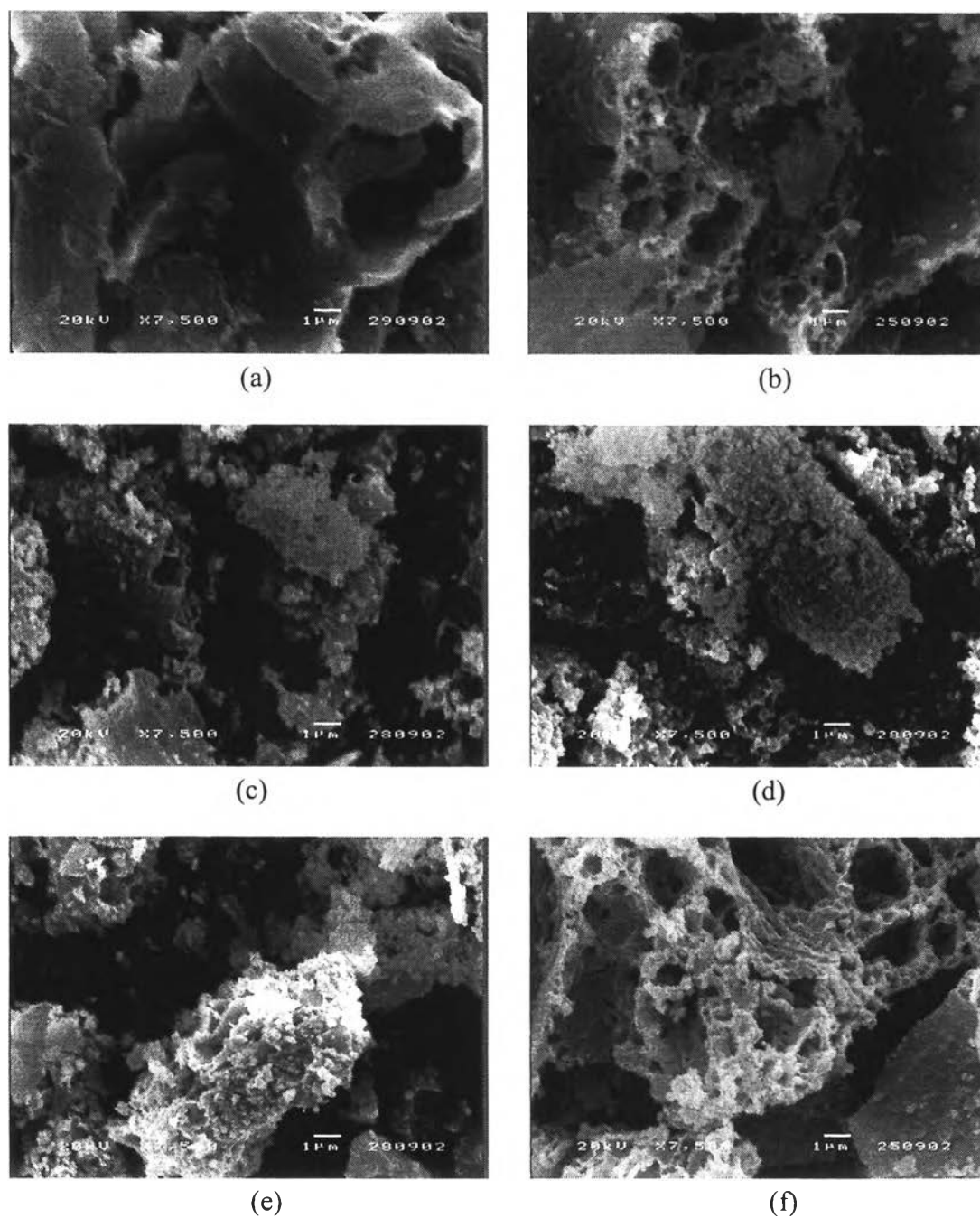
Figure 4.6 Effect of heat treatment on ceria oxide (acid:alkoxide:water = 0.8:1:55) calcined for 1 hr. at (a) 573 K, (b) 673 K, (c) 773 K, (d) 873 K, (e) 973 K, and (f) 1073 K.
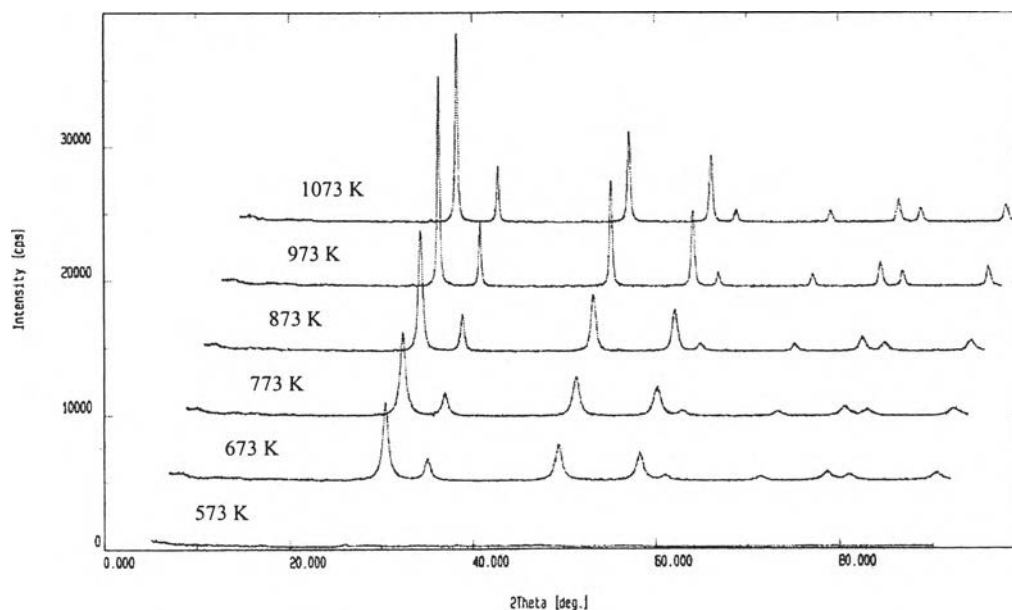
**Figure 4.7** XRD patterns of ceria oxides prepared at the acid : alkoxide : water of 0.8:1:55 and calcined at different temperatures for 1 hr.

X-ray diffraction was used for crystal structure determination. As shown in Figure 4.8, at 400°C the cubic pattern of cerium dioxide is identifiable, but it exhibits broad and low intensity peaks, the characteristics of low crystallines. As the calcination temperature is increased, these peaks become sharper and more intense reflecting an increase in crystallinity and average particle size within the material. The set of peaks were identified and indexed by comparison with literature data, as CeO_2.

The effects of water ratio were examined by performing a similar set of experiments. At constant temperature 673 K, 773 K and 873 K, the calcination time varied from 1 to 7 hours. X-ray diffraction and SEM. shown that as the calcination time is increased, no effect on crystallinity but morphology changed. Surface areaand pore volume collapse did occur with higher temperature and longer time of calcination process. (Figure 4.8, Figure 4.9, Figure 4.10, and Figure 4.11).
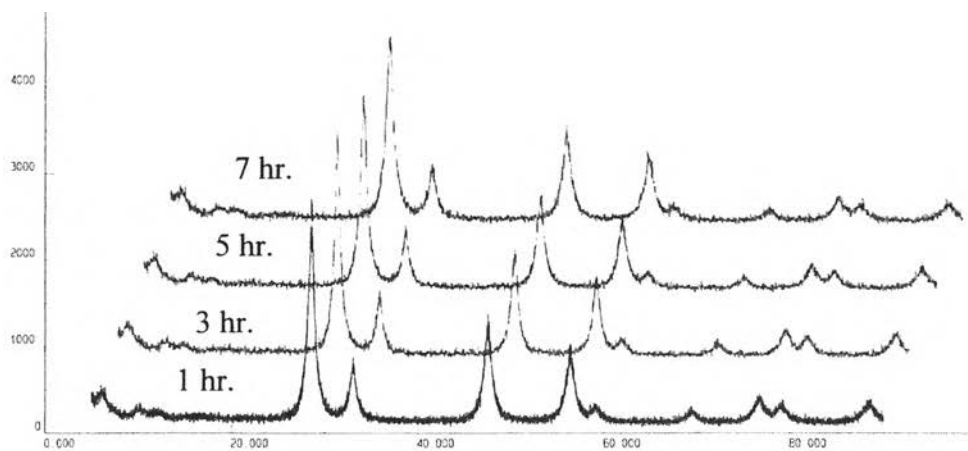
(a)
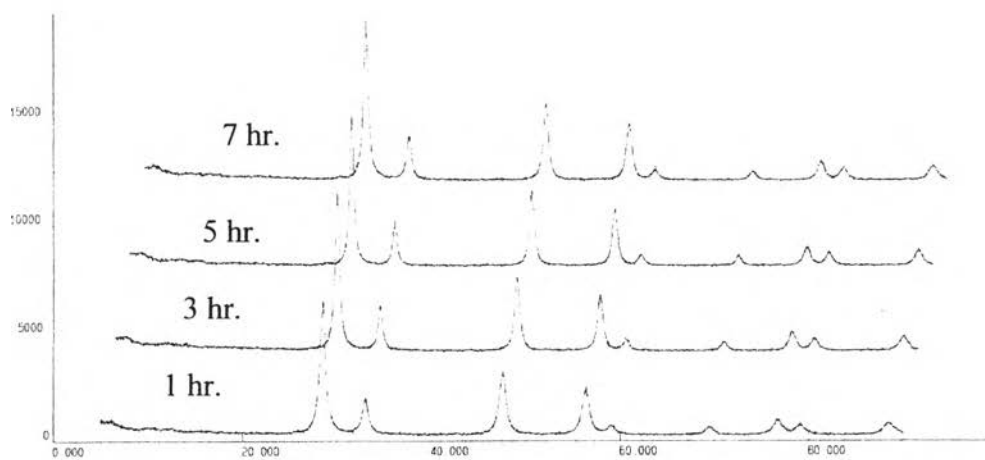
(b)
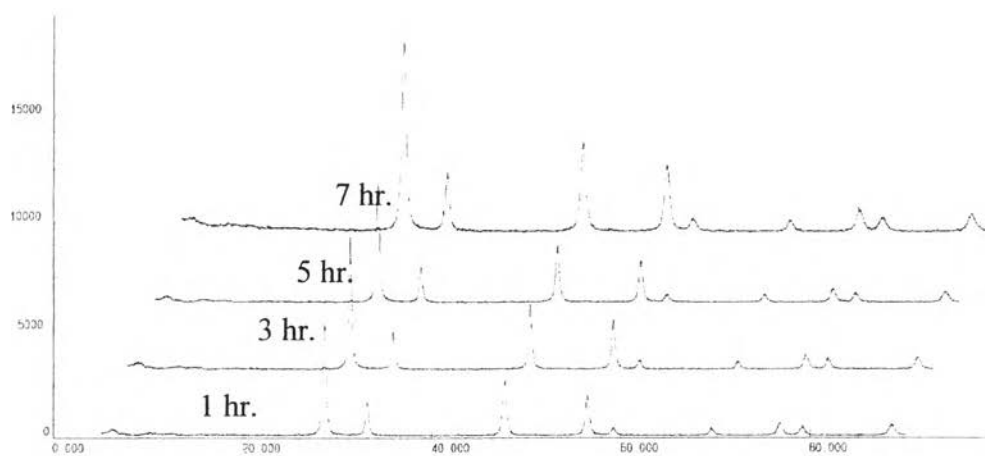
(c)

Figure 4.8 XRD patterns of ceria oxides prepared at the acid : alkoxide : water of 0.8:1:55 and calcined at different cacination time : (a) cacination temperature = 673 K, (b) cacination temperature = 773 K, (c) cacination temperature = 873 K.
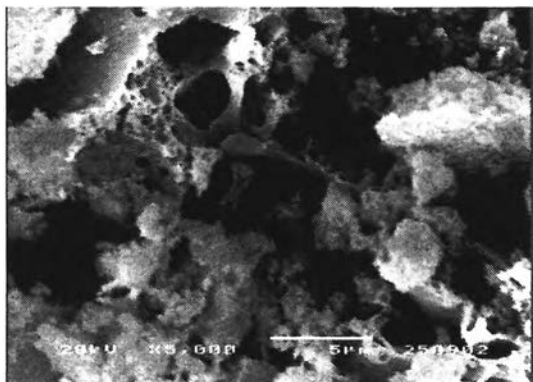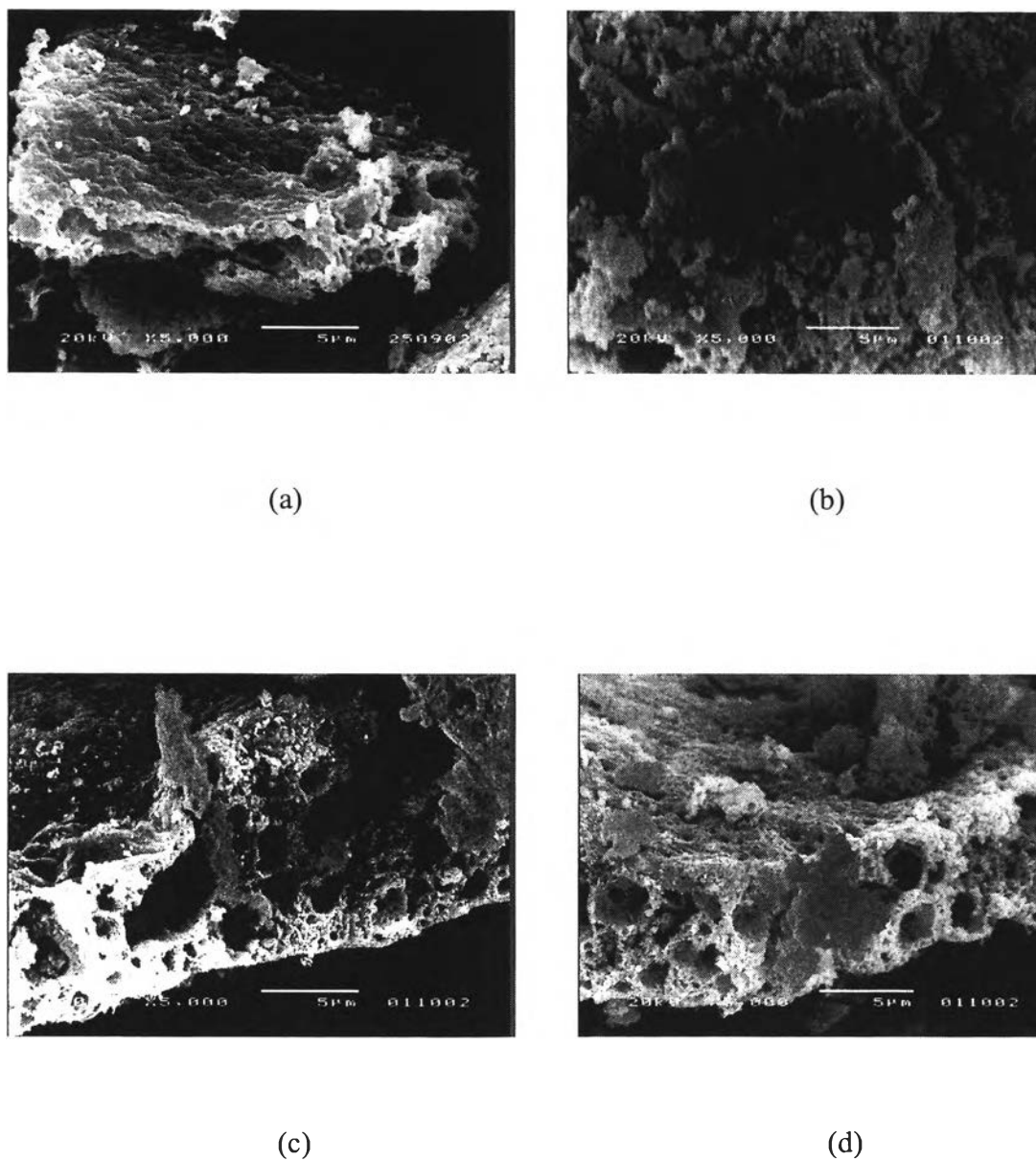
(a)
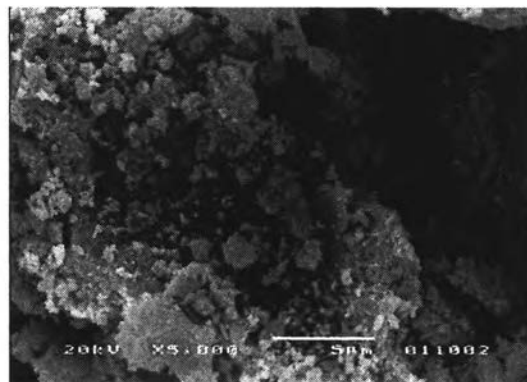
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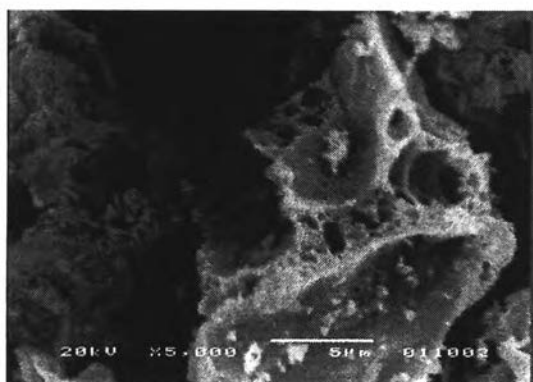
(c)
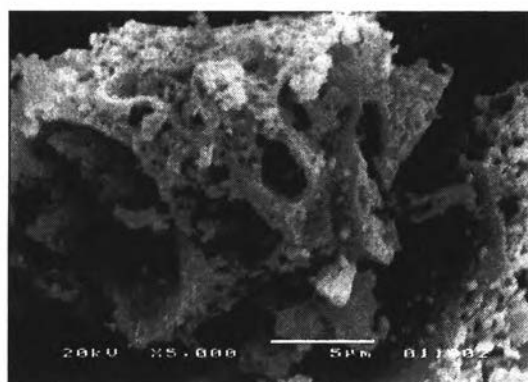
(d)

FIGURE 4.9 Effect of heat treatment on ceria oxides (acid : alkoxide : water = 0.8:1:55) calcined at 673 K for (a) cacination time = 1 hr, (b) cacination time = 3 hr, (c) cacination time = 5 hr, (d) cacination time = 7 hr.

(a)

(b)

(c)

(d)

Figure 4.10 Effect of heat treatment on ceria oxides (acid : alkoxide : water = 0.8:1:55) calcined at 773 K for (a) cacination time = 1 hr, (b) cacination time = 3 hr, (c) calcination time = 5 hr, (d) cacination time = 7 hr.

(a)

(b)

(c)

(d)

Figure 4.11 Effect of heat treatment on ceria oxides (acid : alkoxide : water = 0.8:1:55) calcined at 873 K for (a) cacination time = 1 hr, (b) cacination time = 3 hr, (c) cacination time = 5 hr, (d) cacination time = 7 hr.

4.3 Sol-gel transition

From the series of rheological measurements during the gelation process, the gel point could be defined by a scaling relation between dynamic moduli and frequency:

$$G'(\omega) \;=\; A\omega^{n'} \quad (1) \qquad \text{and}$$

$$G''(\omega) \;=\; B\omega^{n''} \quad (2)$$

at a frequency- independent loss tangent,

$$\tan\delta \quad = \; G''/G' \quad (3)$$

For each time point, it can generate a pair of viscoelastic exponents; n' and n" from the frequency dependence of G' and G", and observe a crossover where n' = n" = n[22].

The viscoelastic properties of four different HCl : alkoxide systems (molar ratio 1.1, 1.0, 0.9, and 0.8, respectively) were studied. The gel for chemically gelling systems can be determined by observation of a frequency-independent value of tan δ versus gelation time. The results in value of tan δ with time as shown in figure 4.12 became frequency independent at a particular gelation time. The lowest gelation time was at 0.8 molar ratio of HCl : alkoxide at 868s, tan δ = 0.2, at molar ratio of HCl : alkoxide = 0.9 galation time = 931s, tan δ = 0.19, and then at molar ratio of HCl : alkoxide = 1.0 galation time =1183s, tan δ = 0.17, and the highest at gelation time at HCl : alkoxide molar ratio = 1.1 gelation time = 5206s, tan δ = 106.

An alternative method to determine gel points is by plotting the apparent viscoelastic exponent n' and n" (G' α $\omega^{n'}$, G" α $\omega^{n''}$) which show an example of 0.9 molar ratio as in figure 4.13 obtained from the approximate scaling laws of the frequency dependence of G' and G" at times removed from the gel point, and observing a crossover where n' = n" = n. The points of the intersection (t_{gel}) were the same as those observed from the plot of tan δ with time.
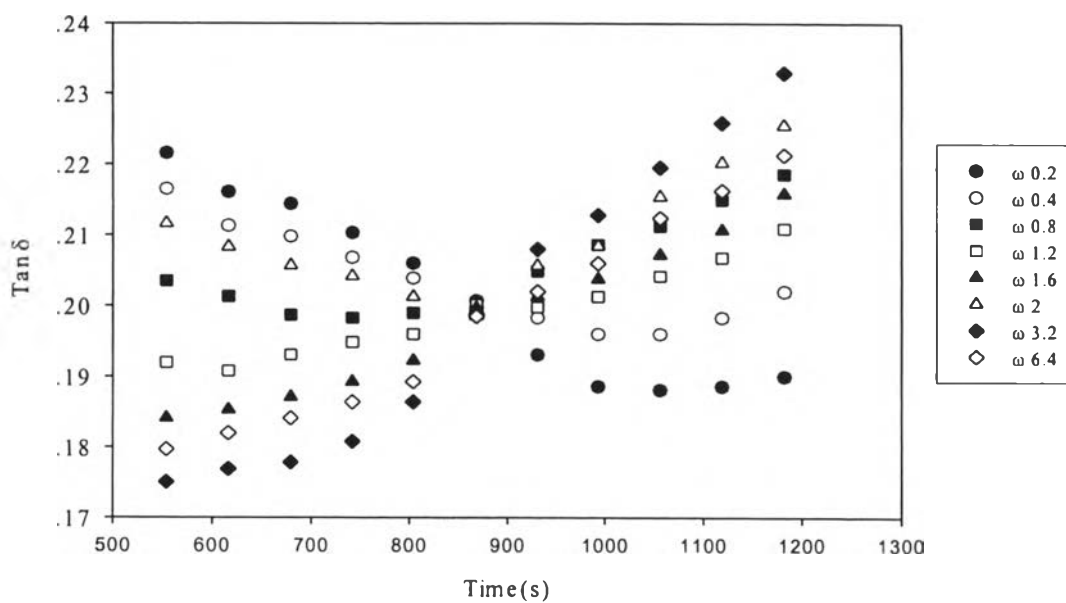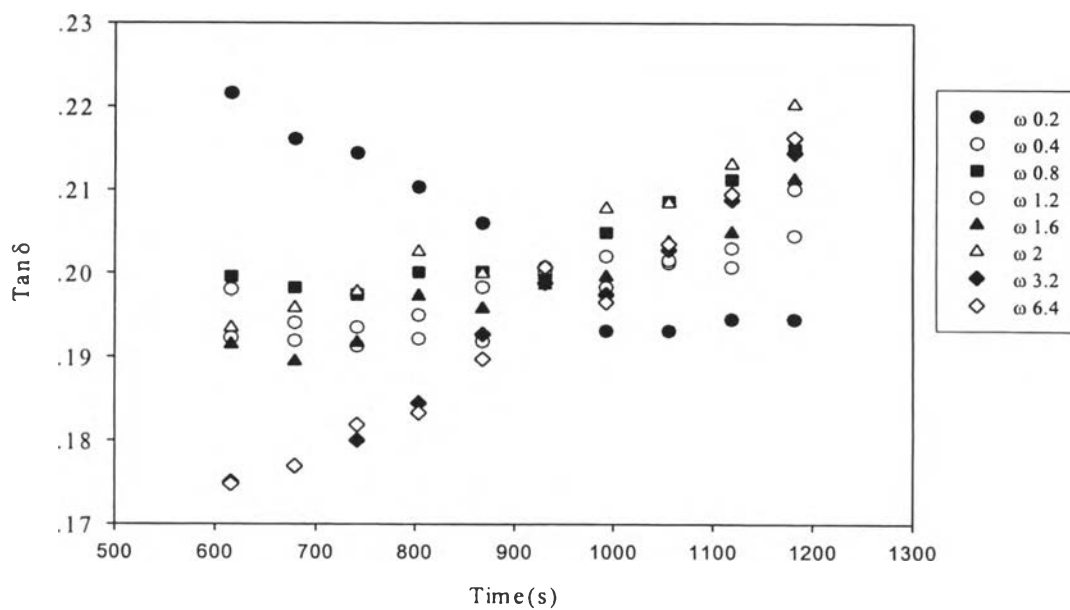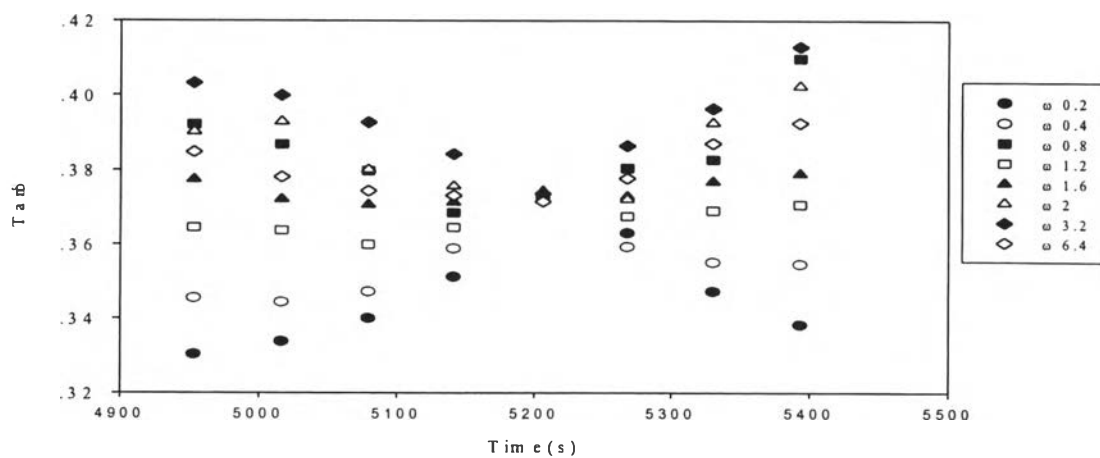
(a)

(b)

Figure 4.12 tan δ vs time : (a) acid : alkoxide molar ratio = 0.8, (b) acid : alkoxide molar ratio = 0.9, (c) acid : alkoxide molar ratio = 1.0, (d) acid : alkoxide molar ratio = 1.1.
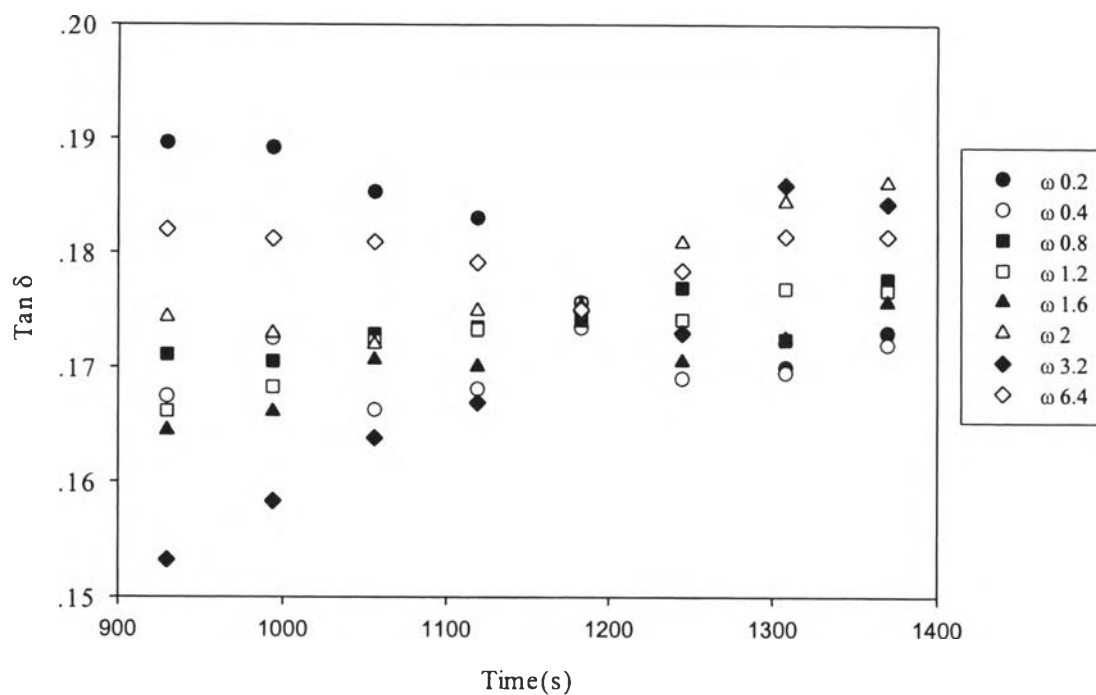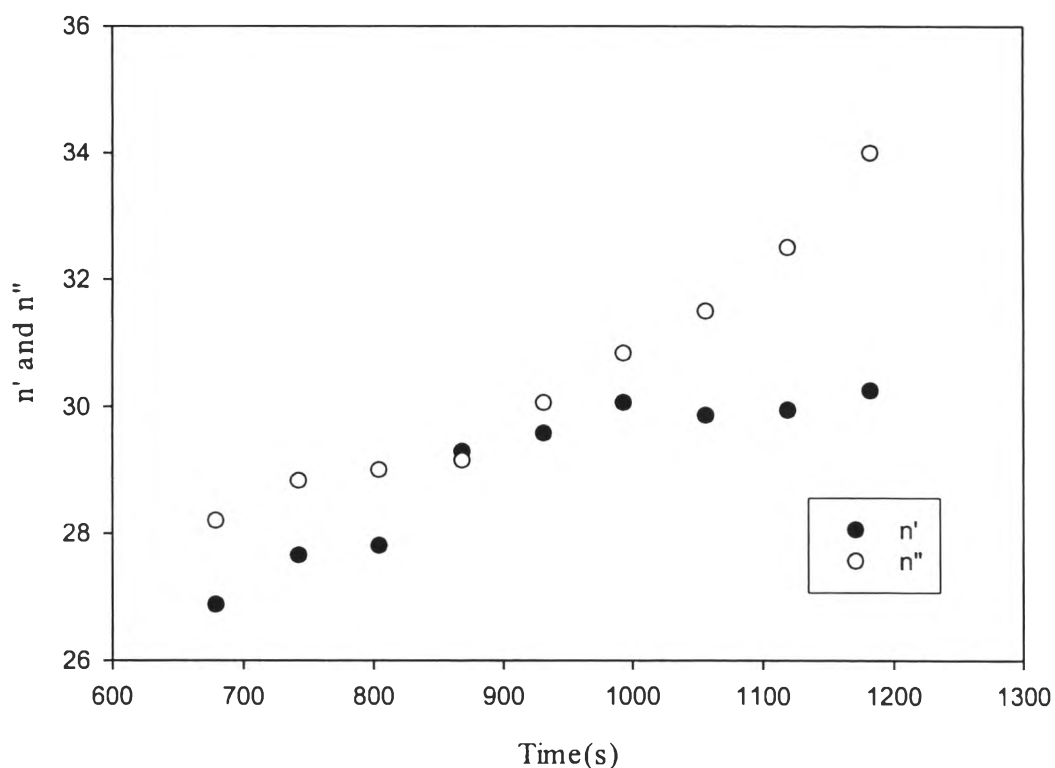
(Cont.)

(c)

(d)

Figure 4.12 (Continued) tan δ vs time : (a) acid : alkoxide molar ratio = 0.8, (b) acid : alkoxide molar ratio = 0.9, (c) acid : alkoxide molar ratio = 1.0, (d) acid : alkoxide molar ratio = 1.1.

Figure 4.13 n', n" vs time of ceria gel (acid : alkoxide : water molar ratio = 0.9 :1:50).

The different stages of the critical moments near the gelation were observed by the plot between G', G" (Pa) with ω (rad/s) before gel point, at gel point, and after gel point of 0.8 molar ratio Figure 4.14 The trend is the same for all the investigated systems which G' values were higher than G" and both values always increased with time. As is well known, both G' and G" could exhibit a power law dependence on applied frequency, at gel point (t_{gel}) n' = n" = n_{gel} and the power-law plots for G' and G" were parallel. From Figure 4.15, the plot of G' and G" with frequencies at the gel point of all defferent acid : alkoxide ratios showed that, the viscoelastic exponent of the systems was highest at 1.1 molar ratio (0.257), then 1.0 ratio (0.180), 0.9 ratio (0.160), and lowest at 0.8 molar ratio (0.151). From the results indicating that 1.1 molar ratio gel was more viscoelastic (i.e. less elastic) at the gel point and the 0.8 molar ratio had the most elastic and stronger cross-linked structure. Variation in G' and G" with applied frequency near the gel point are illustrated. The storage moduli

of the third stage (after gel point) increased in large scale from those before gel point and at gel point but the loss moduli changed in small scale.

The time dependence of the storage moduli G' and loss moduli G''. The G' value were always higher than G'' in every condition, therefore the value of G' predominate over the value of G''. Thus we obtained a qualitative estimate of the gelation kinetics from a measurement of the rate of growth of G' at low deformation frequency. We estimated select the gelation rate as the highest value of the modulus, G' (ω = 1.2), divided by the elapsed time. Thus, for sample 0.8 molar ratio we obtained $\Delta G'/\Delta t$ = 0.75 dynes/cm^{2}sec. At early stages of hydrolysis, the G' values were much larger than G'', i.e. the solutions are predominately elastic in behavior. The acid act as a catalyst to hydrolyze the alkoxide and protonate the alkoxy ligands. Thus, the elimination of this leaving group is no longer the rate-limiting step, and as a result the hydrolysis occurs rapidly. In the case of highest acidity (1.1 molar ratio), the gelation time was highest which suggesting that cluster growth and the network formation occur very slowly. The larger amount of acid not only hydrolyze but also strongly inhibit the condensation process, thus the network cannot form so easily.
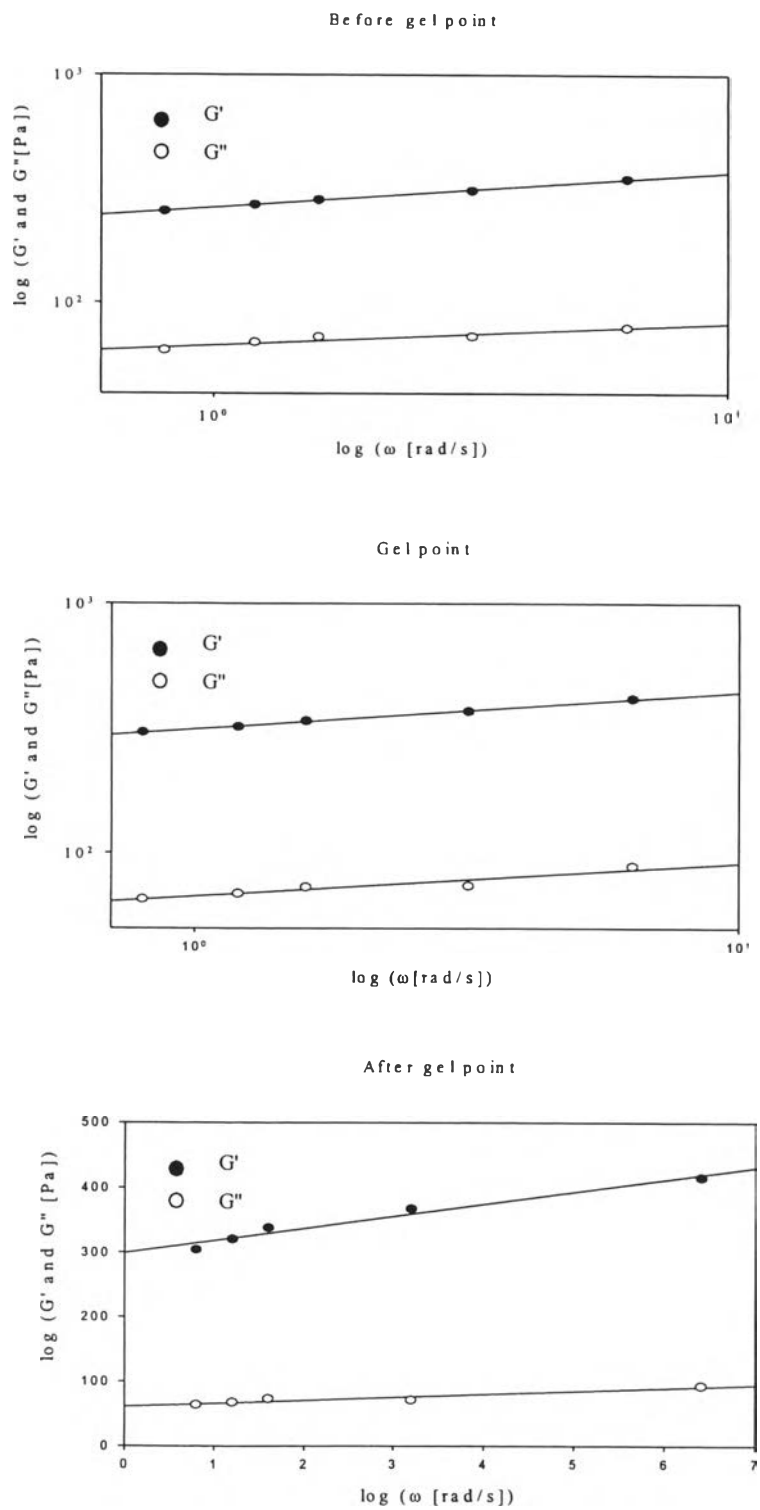
Figure 4.14 log G' and G" vs frequency of ceria gel (acid : alkoxide : water molar ratio = 0.8 :1:50).
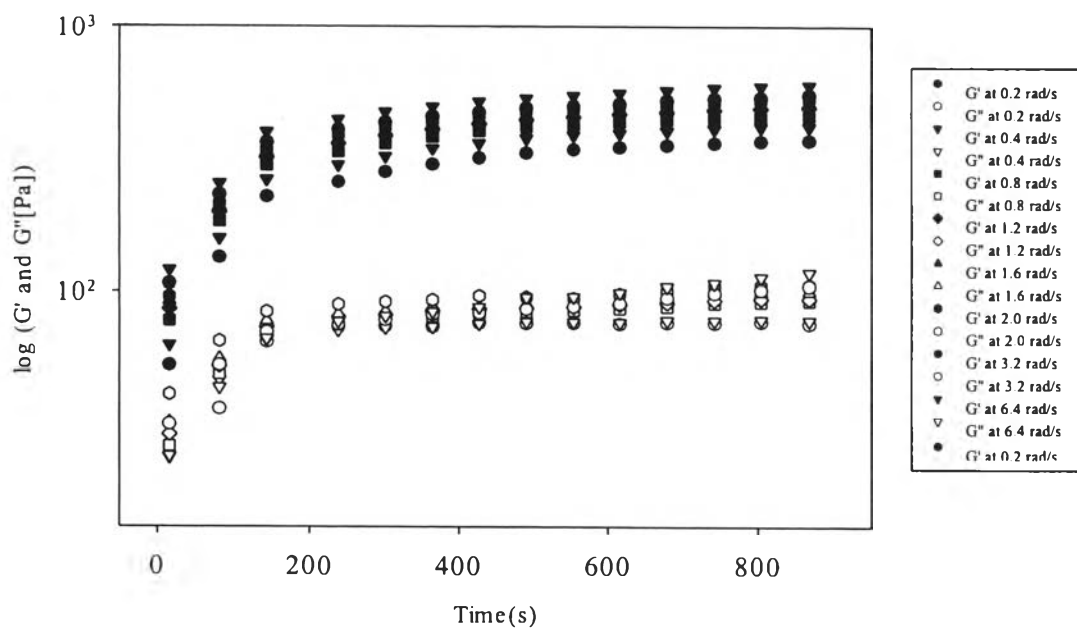
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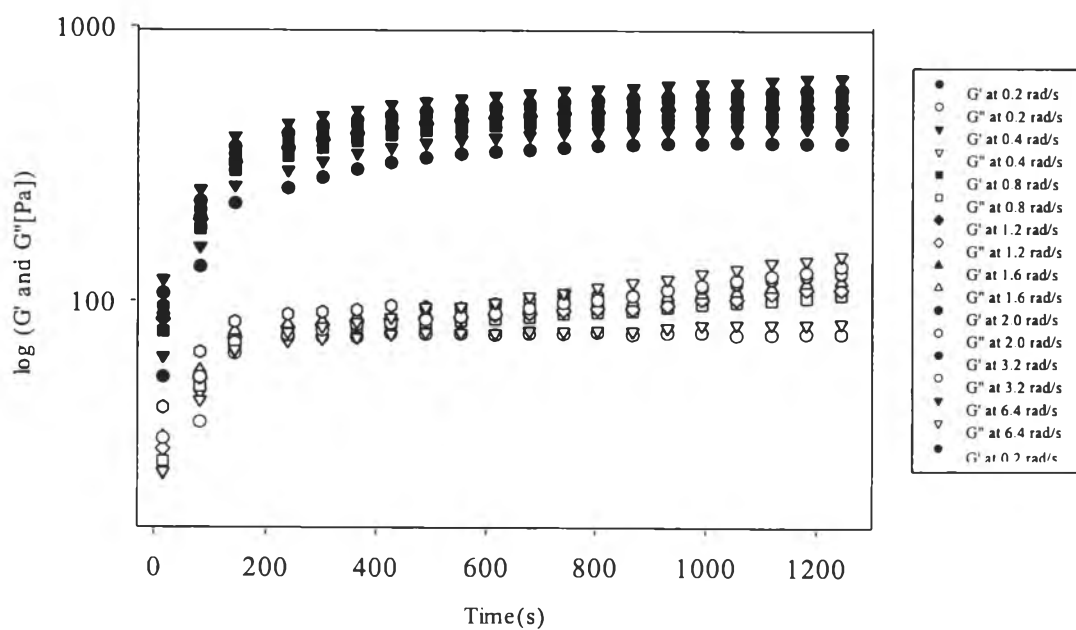
(b)

Figure 4.15 log (G' and G" [Pa]) vs time of Ceria gel : (a) acid : alkoxide molar ratio = 0.8, (b) acid : alkoxide molar ratio = 0.9, (c) acid : alkoxide molar ratio = 1.0, and (d) acid : alkoxide molar ratio = 1.1. (Cont.)
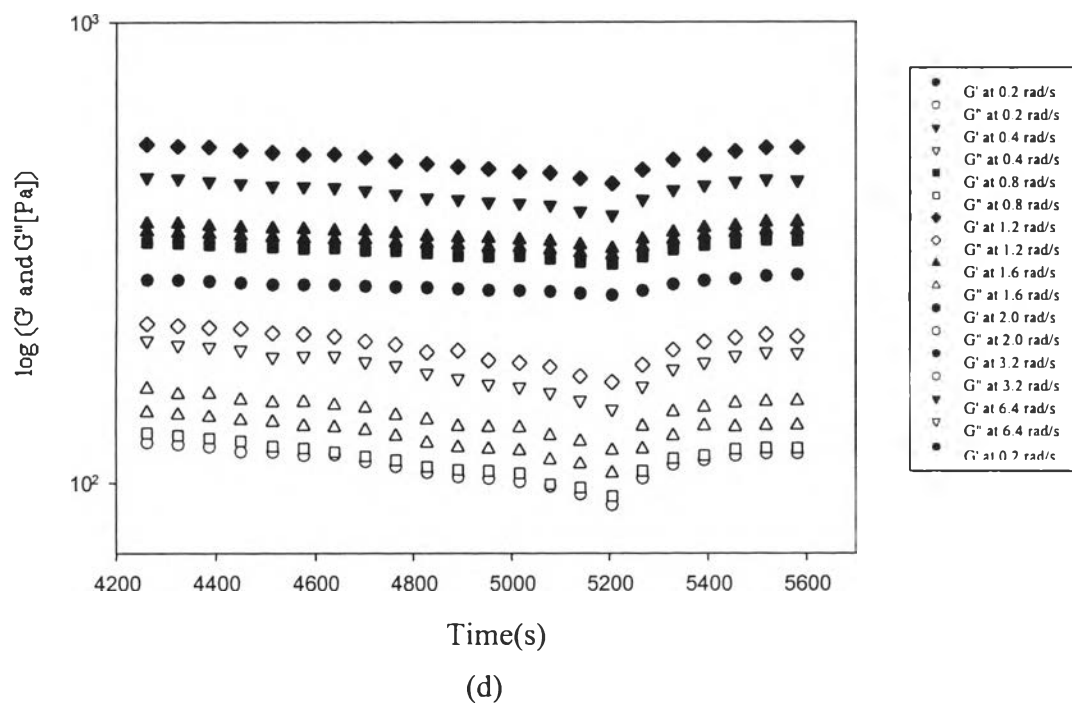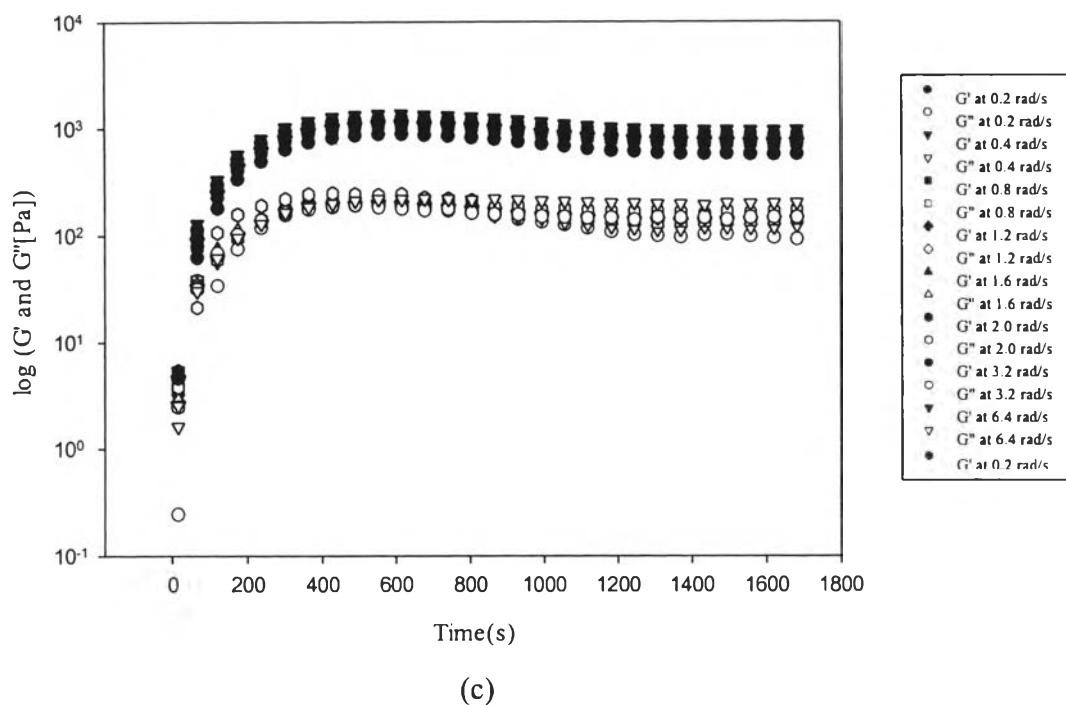
(c)

Time(s)

(d)

Figure 4.15 (Continued) log (G' and G" [Pa]) vs time of Ceria gel : (a) acid : alkoxide molar ratio = 0.8, (b) acid : alkoxide molar ratio = 0.9, (c) acid : alkoxide molar ratio = 1.0, and (d) acid : alkoxide molar ratio = 1.1.

From the tan δ with time as Figure 4.16, the gelation times of H_2O : alkoxide at molar ratio of 50, 55, 60 and 65 were observed. At the lowest molar ratios of H_2O : alkoxide, the gelation time were 868s (50 ratio of H_2O:alkoxide) which the hydrolysis rate is higher than condensation rate. At molar ratio 55, the gelation time was lowest (208s) and the gelation times were higher again at molar ratio 60 and 65 (774s. and 1494s). Although increased value of H_2O generally promote hydrolysis, when H_2O increased while maintaining a constant solvent which is HCl : alkoxide molar ratio, the alkoxide concentration is reduced. This in turn reduces the hydrolysis and condensation rates, resulting in longer gel times. Figure 4.17 and Figure 4.18 showed the G' and G" with frequencies at gel point of all H_2O : HCl ratio. At 65 molar ratio, the viscoelastic exponent was highest (0.220), then 50 ratio (0.151), 60 ratio (0.135), and at 55 ratio (0.127), respectively. Similarly, as the value of tan δ at t_{gel}, tan δ of 55 ratio was significantly lowest and suggested that this ratio had the most elastic than other H_2O : HCl ratios.
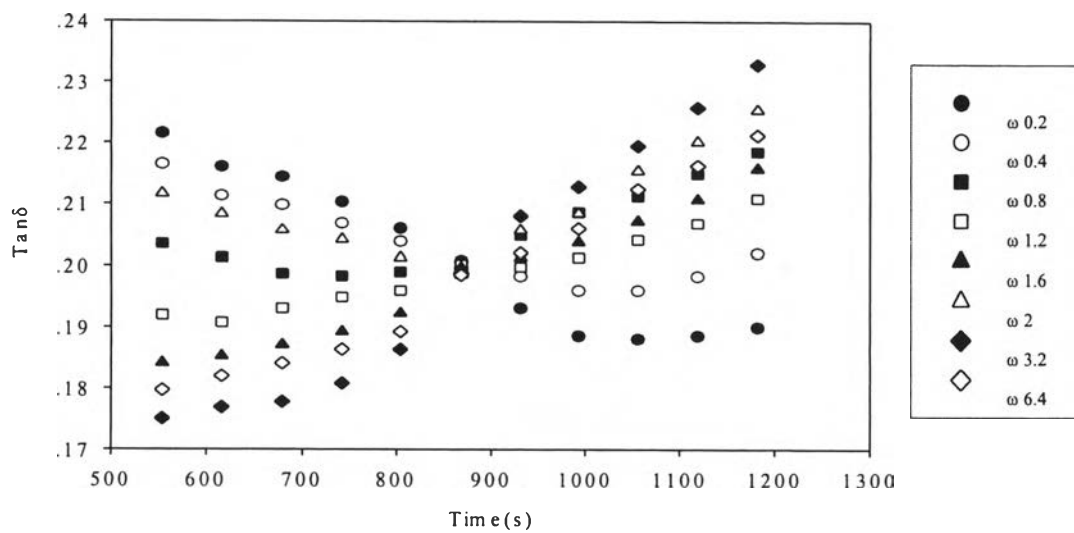
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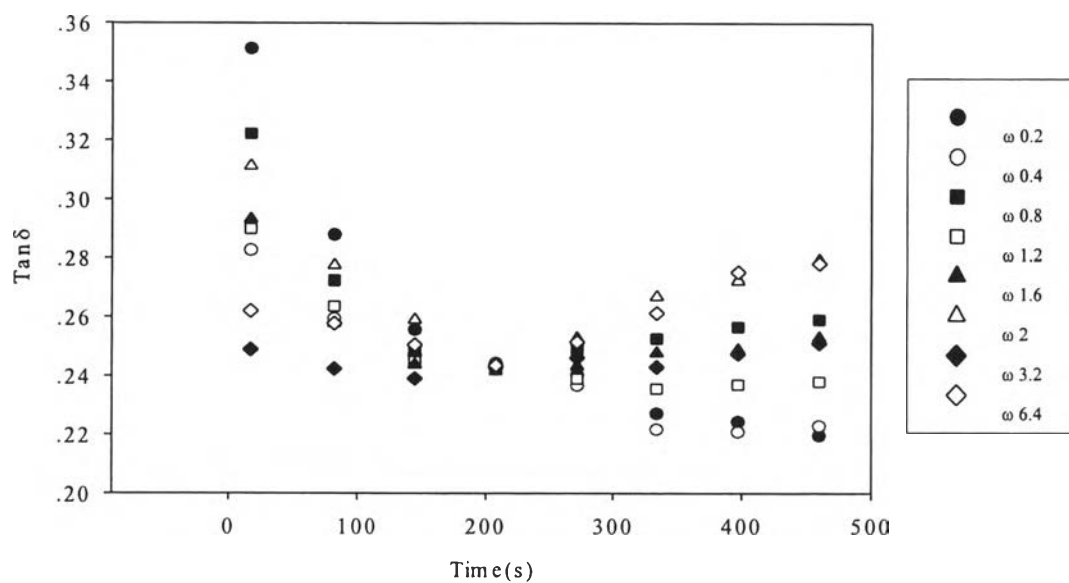
(b)

Figure 4.16 tanδ vs time of Ceria gel : (a) H_2O : alkoxide = 50 : 1, (b) H_2O : alkoxide = 55 : 1, (c) H_2O : alkoxide = 60 : 1, and (d) H_2O : alkoxide = 65 : 1.

(Cont.)
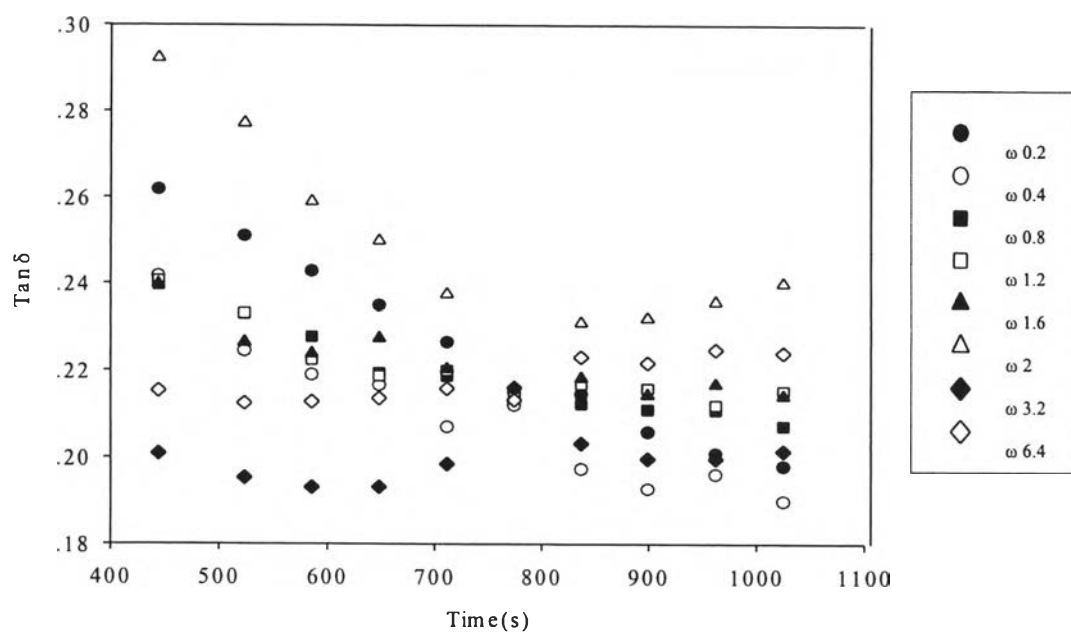
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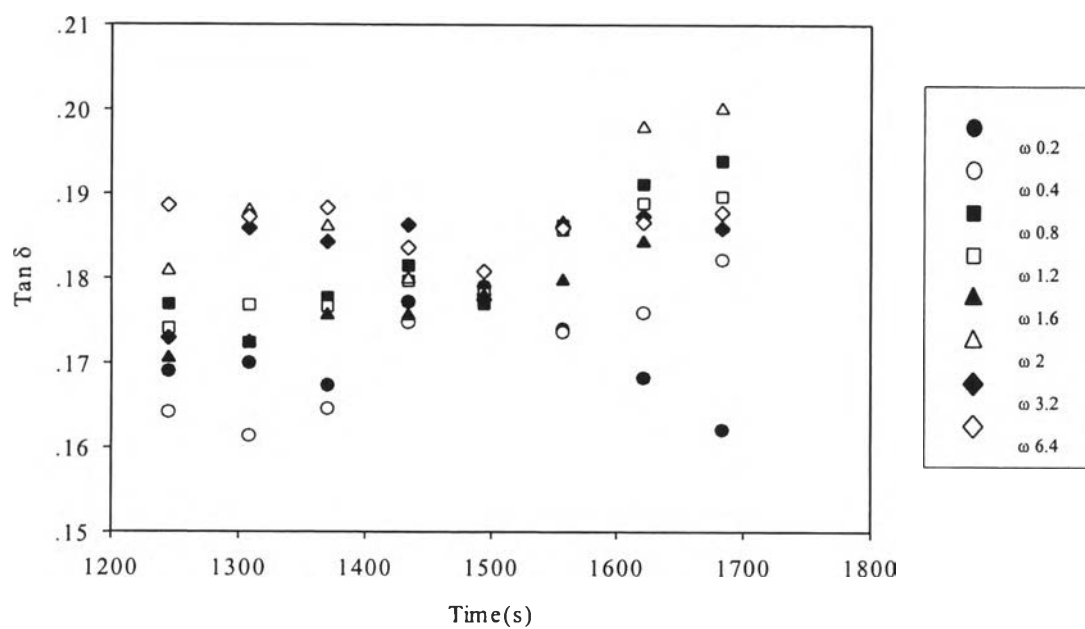
(d)

Figure 4.16 (Continued) tanδ vs time of Ceria gel : (a) H_2O : alkoxide = 50 : 1, (b) H_2O : alkoxide = 55 : 1, (c) H_2O : alkoxide = 60 : 1, and (d) H_2O : alkoxide = 65 : 1.
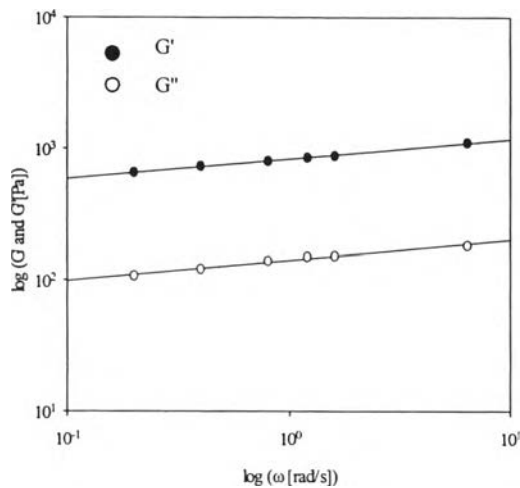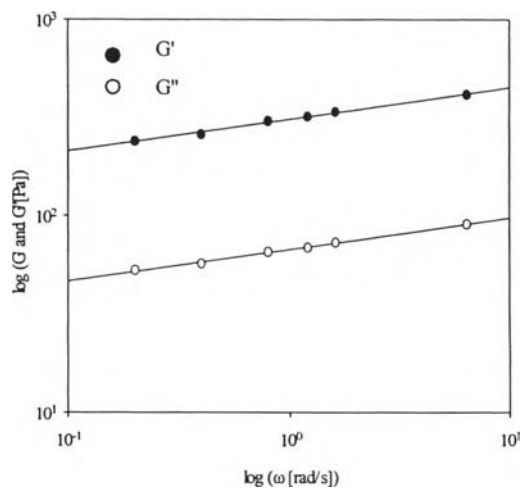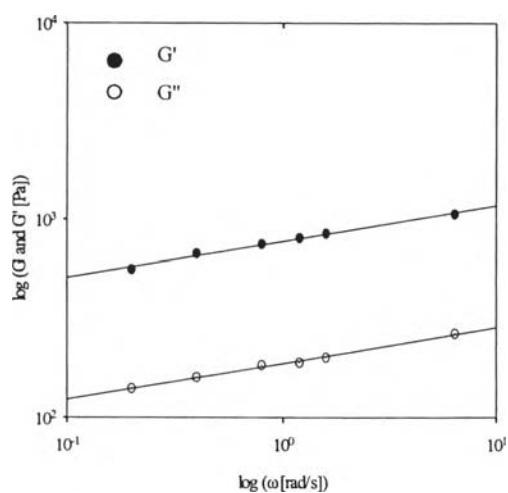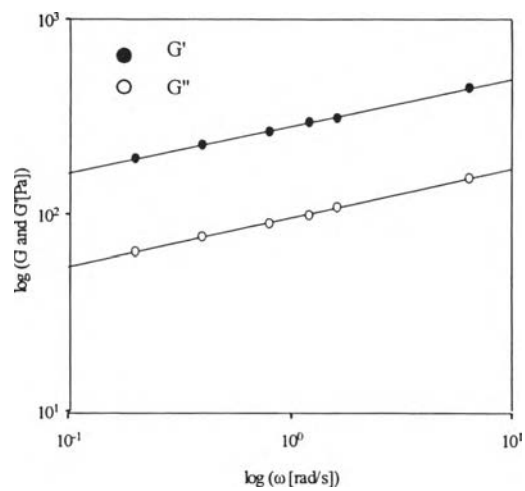
Figure 4.17 log (ω [rad/sec]) vs log (G' and G" [Pa]) : (a) alkoxide : Acid = 1:0.8, (b) alkoxide : Acid = 1:0.9, (c) alkoxide : Acid = 1:1.0, and (d) alkoxide : Acid = 1:1.1.
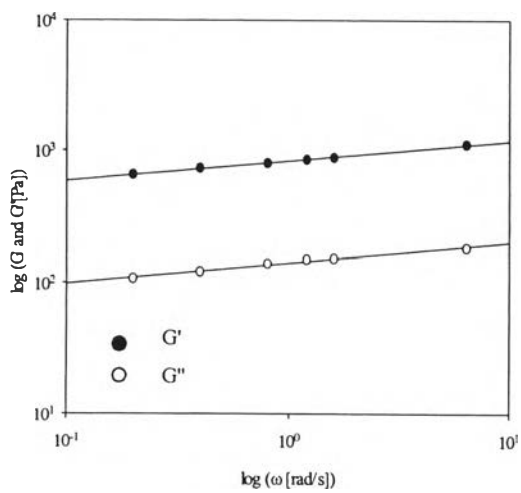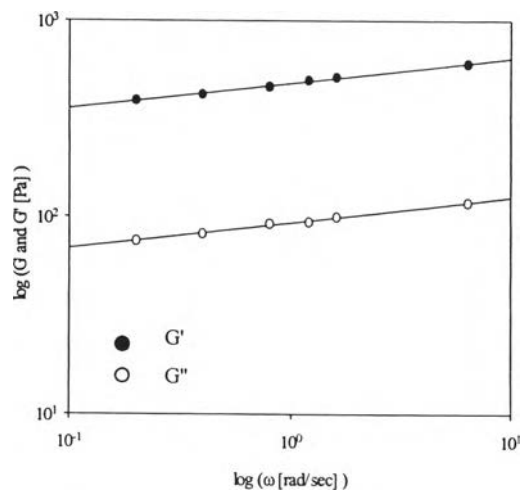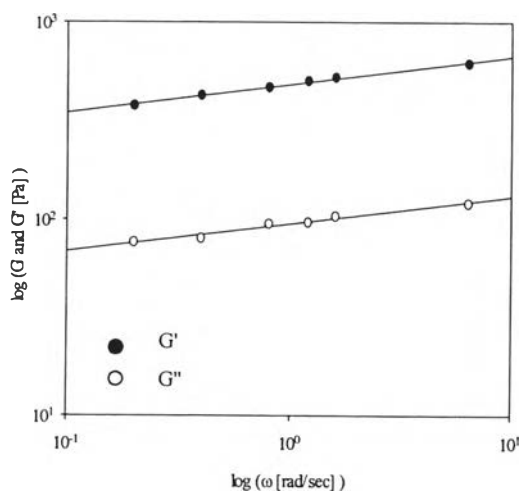
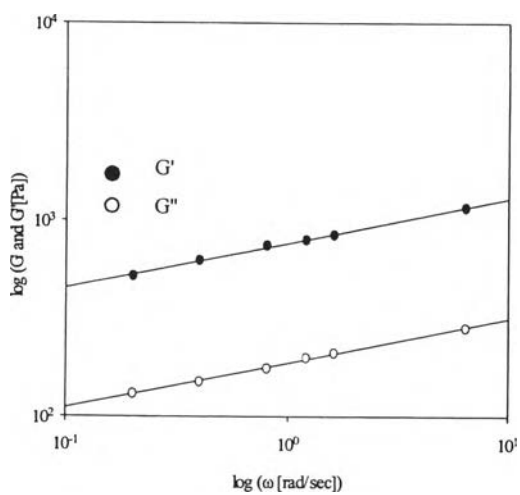**Figure 4.18** log (ω [rad/sec]) vs log (G' and G" [Pa]) : (a) alkoxide : H_2O = 1:50, (b) alkoxide : H_2O = 1:55, (c) alkoxide : H_2O = 1:60, and (d) alkoxide : H_2O = 1:65.