

CHAPTER VI
STRUCTURAL AND CRYSTALLIZATION OF HIGH Ti LOADED TS-1
ZEOLITE

Abstract

The TS-1 with high Ti loading was successfully synthesized using low cost and moisture-stable precursors, titanium glycolate and silatrane. The microwave instrument was used as a heating source for synthesis. The effect of the compositions (TPA⁺, NaOH, H₂O) and conditions (aging time, reaction temperature, reaction time) were studied. The Si:Ti molar ratios were varied from 100.00-5.00 and the ability of Ti incorporated into the zeolite framework was studied. The XRD, FT-IR, SEM and DR-UV were used to characterize the TS-1 samples and all samples showed the characteristic of MFI type. The small amount of extra-framework titanium dioxide was also identified at 5.0 Si:Ti molar ratio. The photocatalytic decomposition of 4-NP was used to test the activity of TS-1 samples and the results of all samples showed high efficiency in PCD.

Keywords: Photocatalytic decomposition, Silatrane, Titanium glycolate, TS-1 and Zeolite

Introduction

Titanium silicate-1 (TS-1), a Ti-containing zeolite with the MFI structure, is a high selective and active crystalline microporous heterogeneous oxidation catalyst employing H_2O_2 under mild conditions. The titanium in TS-1 isomorphously replaces silicon in a tetrahedral site of the MFI silicate lattice. It combined the advantages of the high coordination ability of Ti^{4+} ions with the hydrophobicity of the silicate framework, while retaining the spatial selectivity and specific local geometry of the active sites of the molecular sieve structure [1]. The catalytic properties of titanosilicate are unique with a variety of liquid-phase oxidation such as phenol hydroxylation, olefin epoxidation, cyclohexanone ammoximation and the oxidation of saturated hydrocarbons and alcohol [2,3]. With H_2O_2 , solvolysis produces $TiOOH$ and $SiOH$ with the former giving rise to the active catalytic oxidation center.

After year 1983 which Taramasso *et al* [4] reported the hydrothermal synthesis of TS-1 for the first time, there are many researches tried to increase the amount of Ti^{IV} in the zeolite framework. A major problem often encountered the synthesis of TS-1 molecular sieve is the precipitation of oxide of the titanium outside the lattice framework, leading to samples, inactive for oxidation reactions [5]. The synthesis of materials containing isolated tetrahedral Ti is rather difficult given its strong tendency to polymerize in aqueous systems which often resulting the formation of separate titanium dioxide phase [1]. Two methods to synthesize were described in the original patent using different Si sources, tetraethylorthosilicate (TEOS) and Ludox colloidal silica. TS-1 is usually synthesized using tetrapropylammonium hydroxide (TPAOH) solution, which acts as the structure directing agent and provides the alkalinity necessary for the crystallization of the zeolite [6]. From many previous works, maximum amount of Ti^{IV} that can be incorporated in the zeolite framework is at Si:Ti less than 35 [1, 3, 6]. Furthermore, another attempt to achieve a high degree of substitution ($Si/Ti = 10, 15, 30$) but still has problem of Ti incorporated in framework.

Microwave-assisted-hydrothermal synthesis is the process has been used for the rapid synthesis of numerous ceramic oxides and porous materials. It offers many advantages over conventional synthesis including microwave can rise the

temperature of the reactant to a desired range quickly in a few minutes, homogeneous nucleation, fast supersaturation by the rapid dissolution of precipitated gels and shorter crystallization time than conventional method. The heat is supposedly induced by the friction of molecular rotation enhanced by microwave irradiation, thus, it is possible to heat the reactants selectively and homogeneously from the inside. Furthermore, It is energy efficient and economical [7, 8].

In this work, we synthesized the TS-1 zeolite from moisture stable and low cost starting materials, silatrane and titanium glycolate, for a source of silica and titanium dioxide and TPABr as a template. The hydrothermal treatment was microwave heating and varies amount of Ti incorporated in the zeolite framework was studied. The samples were characterized by XRD, SEM, FT-IR and DR-UV. The photocatalytic decomposition of 4-NP was used to test the activity of TS-1 samples.

Experimental

Materials

Titanium dioxide (surface area 12 m²/g) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Malinckrodt Baker, Inc. (USA) and purified by fractional distillation at 200°C under nitrogen at atmospheric pressure, before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile was purchased from Lab-Scan Company Co. Ltd. and purified by distilling over calcium hydride powder. 4-Nitrophenol was purchased from Sigma-Aldrich Chemical Co. Inc. (USA).

Instrumental

Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm⁻¹ using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of 10°C/min over 30°-800°C temperature range. The mass spectrum was obtained on a Fison Instrument (VG Autospec-ultima 707E) with VG data system,

using the positive fast atomic bombardment mode (FAB⁺-MS) with glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration. ¹³C- solid state NMR spectroscopy was performed using a Bruker AVANCE DPX-300 MAS-NMR. Elemental analysis (EA) was carried out on a C/H/N Analyser (Perkin Elmer PE2400 series II).

Preparation of titanium glycolate

The procedure adopted followed previous work [9]. A mixture of TiO₂ (2g, 0.025 mol) and TETA (3.65g, 0.0074 mol) was stirred vigorously in excess EG (25 cm³) and heated to 200°C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO₂. The excess EG and TETA were removed by vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FTIR, ¹³C-solid state NMR, EA, FAB⁺-MS, and TGA.

FTIR: 2927-2855 cm⁻¹ (νC-H), 1080 cm⁻¹ (νC-O-Ti bond), and 619 cm⁻¹ (νTi-O bond). ¹³C-solid state NMR: two peaks at 74.8 and 79.2 ppm. EA: 28.6% C and 4.8% H. FAB⁺-MS: approximately 8.5% of the highest m/e at 169 of [Ti(OCH₂CH₂O)₂]H⁺, 73% intensity at 94 of [OTiOCH₂] and 63.5% intensity at m/e 45 of [CH₂CH₂OH]. TGA: one sharp transition at 340 °C and 46.95% ceramic yield corresponding to Ti(OCH₂CH₂O)₂.

Preparation of silatrane

A mixture of Si(OH)₂ (6g, 0.1 mol) and TEA (18.648g, 0.125 mol) was stirred vigorously in excess EG (100 cm³) and heated to 200°C for 10 h. The resulting solution was vacuum to remove EG to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FTIR, FAB⁺-MS, and TGA.

FT-IR : 3422 cm⁻¹ (ν O-H), 2986-2861 cm⁻¹ (ν C-H), 2697 cm⁻¹ (ν N-Si), 1459-1445 cm⁻¹ (δ C-H), 1351 cm⁻¹ (δ C-N), 1082 cm⁻¹ (δ Si-O-C), 579 cm⁻¹ (ν N-Si). FAB⁺-MS: approximately 100% of the m/e at 174 of N[CH₂CH₂O]₃Si⁺, 11.3% intensity at 236 of H⁺OCH₂CH₂OSi[OCH₂CH₂]₃N, 2.6% intensity at 323 of H⁺[HOCH₂CH₂]₂NCH₂CH₂OSi[OCH₂CH₂]₃N and 0.04% intensity at m/e 409 of N[CH₂CH₂O]₃H⁺SiOCH₂CH₂OSi[OCH₂CH₂]₃N.

Preparation of TS-1 zeolite

The hydrothermal syntheses were carried out using microwave irradiation. The TS-1 solution with the initial molar composition of gel equal to $\text{SiO}_2:0.1\text{TiO}_2:0.1\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$. The effect of conditions was studied by varying the aging time (20, 60, 70, 90, 110, 130, 150, 170h), reaction time (5, 10, 15, 20h) and reaction temperature (120, 150, 180°C). The effect of conditions was studied by varied the TPA^+ , NaOH and H_2O . For the study of the Ti incorporated in the zeolite framework, the $\text{SiO}_2:x\text{TiO}_2:0.3\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$ ($x = 0.1, 0.3, 0.5, 0.7, 1.0, 1.3, 1.7, 2.0$) was used. The solution was then aging at room temperature for 110h. After aging, the solution was transferred into Teflon vessel and heated under microwave irradiation at 150°C and at varied reaction time. The TS-1 zeolite was washed several times with distilled water, dried at 60°C overnight and calcined at 550°C for 2h (0.5°C/min).

Photocatalytic decomposition of 4-nitrophenol

The photocatalytic reactions were carried out in the 250 ml batch reactor with a gas inlet and outlet at the flow rate of O_2 gas 20 ml/min. The cooling water jacket was used to control the temperature at 30°C. The suspensions were illuminated by using a Hg Philip UV lamp. The concentration of 4-NP was 40 ppm and the solution was continuous magnetically stirred. The TS-1 zeolite at Si/Ti molar ratios 100.00, 14.29, 7.69 and 5.00 was added in the solution with the concentration of catalyst 0.8 g/l, after that the 10 mmol/l H_2O_2 was dropped. The samples were taken out and analyzed the concentration of 4-NP by Shimadzu UV-240 spectrophotometer.

TS-1 characterization

The TS-1 samples were characterized by various techniques. XRD patterns were characterized using a D/MAX-2200H Rigaku diffractometer with $\text{CuK}\alpha$ radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range between 5° to 50°. Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1} using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. Samples were prepared for SEM analysis by attachment to aluminum stubs, after pyrolysis at

550°C. Prior to analysis, the specimens were dried in a vacuum oven at 70°C for 5 h followed by coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at x7,500 magnification. Diffuse reflectance ultraviolet-visible (DR-UV) spectra were analyzed

Results and Discussion

1. Synthesis of TS-1

The TS-1 is successfully synthesized by microwave hydrothermal treatment using silatrane and titanium glycolate as precursors in the condition with NaOH and TPABr. The XRD pattern (figure 1) shows the characteristic of MFI structure as reported by many literatures [1, 3, 10, 11]. The single peaks at $2\theta = 24.4^\circ$ indicate a change from monoclinic symmetry (silicate) to orthorhombic symmetry (TS-1) [1,12] The FT-IR spectra of TS-1 in the framework Ti-O-Si bond stretching region shows an absorption band located at 960 cm^{-1} (figure2). This band has been also observed in Ti-containing zeolites, being mainly assigned to the stretching mode of $[\text{SiO}_4]$ tetrahedral bond with Ti atoms [13, 14]. However, such assignment has been interpreted in term of Si-OH groups with many defect structures [15]. The bands at 550 and 800 cm^{-1} are assigned to $\delta(\text{Si-O-Si})$ and $\nu(\text{Si-O-Si})$, respectively. The diffuse reflectance spectra as figure3 shows only one absorption band with a maximum at 210 nm, attribute to tetra-coordinated titanium, and there is no peak at 330 nm which is the peak of titanium dioxide extra-framework.

2. Effect of crystallization conditions and compositions of TS-1

2.1 Effect of reaction temperature

The effect of reaction temperature is studied by varying the temperature at 120° , 150° and 180°C . The synthesis formula is $\text{Si}:0.1\text{Ti}:0.4\text{NaOH}:0.1\text{TPA}:114\text{H}_2\text{O}$. Figure4 shows the XRD patterns of all samples, the intensity of peak increases as the reaction temperature. Its mean that when increasing the reaction temperature lead to the higher rate of crystallization. From the SEM micrograph of calcined samples, the crystal size increases with the reaction temperature. At 120°C (figure5a), the crystals have round shape and not uniform ($0.5\text{-}2.5\mu\text{m}$). As increasing the temperature to 150°C (figure5b), the crystals are uniform with cubic structure ($1\mu\text{m}$). The largest

crystal size ($4\mu\text{m}$) is observed at 180°C (figure5c) and indicates larger growth in c direction with hexagonal shape. When rising the temperature to 180°C , the degradation of the organic template is occurred. From the result, the suitable reaction temperature for a smallest and uniformly crystal is at 150°C .

2.2 Effect of reaction time

The $\text{Si}:0.1\text{Ti}:0.4\text{NaOH}:0.1\text{TPA}:114\text{H}_2\text{O}$ formula is used to study the effect of reaction time to the crystallization of TS-1 zeolite. The reaction times are various from 5, 10, 15 and 20 h at reaction temperature 150°C . The results show that at low reaction time the amorphous phase occurs and the conversion to TS-1 zeolite is lower than at higher time. It is mean that increasing the reaction time causes the increasing of the rate of crystallization. The SEM micrograph (figure6) shows the large crystal size ($5\mu\text{m}$) at 5h and the size decreases dramatically to $1.3\mu\text{m}$ at 15h, the crystals have uniformly cubic shape. Increasing the reaction time to 20 h causes the larger crystal size and has a higher growth in b direction.

2.3 Effect of Aging time

The TS-1 samples at varies aging times (20, 60, 70, 90, 110, 130, 150 and 170h) are carried out at $\text{Si}:0.1\text{Ti}:0.4\text{NaOH}:0.1\text{TPA}:114\text{H}_2\text{O}$, reaction temperature 150°C and reaction time 15h. From the SEM micrographs in figure7, at lower aging time, the large crystal sizes are formed with lower conversion to the TS-1 zeolite and present the large amount of amorphous phase. When the time increase, the crystal size become smaller until at aging time 130h the size increase again. The hydrolysis and condensation reaction of silatrane and titanium precursors cause the polymerization to form the network and initially at low aging time the hydrolysis of precursor does not involve all the alkyl ligand therefore some organic ligand still present in the solution. The remaining organic ligand can participate with the organic template and form a primary unit then the primary units are agglomerate and the nucleation occurs. At longer aging time, the large amount of primary particles are occur and resulting in the higher agglomeration and crystallization rate caused the smaller size with higher formation of zeolite after hydrothermal synthesis, which the growth rate are dominant. At longer aging time (130h), the limited of the primary unit formation occur therefore the agglomeration occurs at the former nuclei.

2.4 Effect of NaOH:Si

The effect of NaOH:Si is studied at varying ratio from 0.1 to 1.0 mol ratio at aging time 110h, reaction time 15h and reaction temperature 150°C. At 0.1 mol ratio, the product is amorphous as shown in the SEM micrograph (figure 8a). When increasing the ratio to 0.3, a very large crystal size of TS-1 zeolite is occurred (10µm) with many secondary growths on the crystals (figure 8b). As the Si:NaOH molar ratio increases to 0.4, the uniform and smaller crystals (1.3µm) are formed (figure 8c). Increasing the ratios to 0.5 causes the larger size and at 0.7 molar ratio has many secondary growths on the crystals (figure 8d and 8e). Until at 1.0 molar ratio (figure 8f), the particles loss the cubic shape. The increasing of NaOH causes the increasing in the concentration of reactive species available in solution for zeolite nucleation which NaOH accelerates the hydrolysis rate, after that the condensation occurs and starts to form a zeolite network with greater numbers of nuclei are generated and smaller particle size products are formed (0.3 molar ratio). At large amount of NaOH, the hydrolysis increases and the large crystals with secondary growths are formed (0.5 and 0.7 molar ratios). When increasing to a very high amount of NaOH, the sodium will efficiently occupy the surface of the silica gel particles cause the retardation of the nucleation because the TPA-Silica interaction is greatly reduced. A large part of the silica is in the core of the gel bodies and not accessible for nucleation formation [16].

2.5 Effect of TPA:Si

The steric stabilization of nuclear-sized entities, is also critically dependent on the cation balance. The TPA⁺ cation is widely used in the synthesizing of zeolite, the bulky quaternary ammonium cations adsorbed on to particle surfaces provide steric stabilization, preventing aggregation upon collision [16]. There are many types of template used in the synthesis of zeolite such as TPAOH, TBABr, 1,6-hexanediamine and TPABr. Wang et al.[6] found that the synthesis by using TBABr will produce a favorable effect on the formation of ZSM-11 and synthesize by 1,6-hexanediamine can use only for low titanium content which increasing the amount of titanium leads to a decrease of crystallinity. To decrease the cost of synthesis,

TPAOH is replaced by TPABr. From many works TPABr showed a good selective oxidation reaction [6, 12].

In our work, TPABr is used to synthesize TS-1 zeolite and the effect of TPA^+ is studied at $\text{Si}:0.1\text{Ti}:0.4\text{NaOH}:x\text{TPA}^+:114\text{H}_2\text{O}$ ($x = 0.05, 0.1, 0.2, 0.3, 0.4$ and 0.5). The crystallization conditions are at aging time 110 h, reaction time 15h and reaction temperature 150°C . Figure 9 shows the SEM micrograph represented the study of the effect of $\text{TPA}^+:\text{Si}$ at aging time 110h, reaction time 15h, 150°C and 0.4 Si:NaOH molar ratio. At low molar ratio (0.05), the large crystals are formed ($10\mu\text{m}$). Increasing the amount of TPA^+ causes the decrease of the crystal size ($1.2\mu\text{m}$ at 0.3 molar ratio) but at large amount of TPA^+ , the secondary growths occur (0.4 and 0.5 molar ratios). From the explanation of the Koebler *et al.* [17], the nucleation starts to occur on the surface of the large gel sphere; both TPA^+ and silica are abundance, into the gel sphere. TPA^+ will transport from solution to the crystal/gel interface, the crystal growing and formed a perfected cubic shape. Its mean that if we increase the amount of TPA^+ , it will lead to the higher nucleation as shown here. At higher TPA^+ , the dendritic growth occurs at the surface of zeolite. This is indicative of very high supersaturation.

2.6 Effect of $\text{H}_2\text{O}:\text{Si}$ ratio

The dilution is studied at $\text{Si}:0.1\text{Ti}:0.4\text{NaOH}:0.3\text{TPA}:x\text{H}_2\text{O}$ ($x = 80, 114, 140, 170$ and 200). The reaction time is 15h, 150°C and aging time 110h. From the SEM micrograph as figure 10, at lower $\text{H}_2\text{O}:\text{Si}$ shows a non-uniform crystal structure. As increasing the ratio to 114, the uniform and completely cubic structures are formed but when further increasing to higher ratio the crystal size are larger and have many defects.

2.7 Effect of $\text{Si}:\text{Ti}$ ratio

The effect of Si:Ti on the crystallization of TS-1 is carry out at $\text{Si}:x\text{Ti}:0.4\text{NaOH}:0.3\text{TPA}:114\text{H}_2\text{O}$ ($x = 100.00, 33.33, 20.00, 14.29, 10.00, 7.69, 5.88$ and 5.0). The reaction temperature is 150°C , aging time 110h and reaction times are varied from 15 to 35 h depending on the Ti loading (Table1). We find that at high Ti loading, increasing the reaction time leads to the higher Ti incorporation. Figure 11 illustrates the FT-IR spectra of TS-1 samples A-H. The peak at 960 cm^{-1} attributes to

a stretching mode of an $[\text{SiO}_4]$ unit bonded to a Ti^{4+} ion (O_3SiOTi) [12] represents the incorporation of titanium in the MFI framework. A strong band at 550cm^{-1} is the characteristic of MFI structure [8]. The DR-UV spectra of the samples A-H are shown in figure 12. The strong peak at 210 nm has been assigned to the tetra-coordinate of titanium in the zeolite framework. The broad band peak at 280 nm indicates the partially polymerized hexa-coordinated Ti species, which contain Ti-O-Ti and belong to a silicon-rich amorphous phase [19]. The band at 330 nm, which assigns to the extra-framework anatase phase, is shown as a little peak in sample H. The peaks at both 210 and 280 nm are increase from sample A to H as higher titanium content and the band shift to higher wavelengths at sample with lower Si/Ti ratio because of the higher proportion of hexa-coordinate species. The peak at 280 nm increases stronger than 210 nm at sample F that means the hexa-coordinated Ti species will form at higher titanium loaded. The XRD and SEM of TS-1 samples are shown in figure 13 and 14, all of the samples show the characteristic of TS-1 zeolite with the MFI structure.

3. Photocatalytic decomposition of 4-nitrophenol

From the discussion of Lee *et al* and Lea *et al*. [20, 21], the photocatalytic decomposition of 4-NP was completely in the presence of H_2O_2 and UV irradiation. The photodecomposition of 4-NP is governed by $\cdot\text{OH}$ radical reactions. The $\cdot\text{OH}$ can be easily to formed from titanium-hydroperoxide species. Thus, in our work we carried out the PCD of 4-NP at 1.0 mmol/l of H_2O_2 under UV irradiate. Table 2 shows the results from PCD of 4-NP with TS-1 zeolite at various Si/Ti molar ratios. The PCD increases with the amount of titanium incorporated in the zeolite and the fastest complete decomposition is at 5.0 Si:Ti molar ratio.

Conclusions

The TS-1 with highly titanium incorporated in the zeolite framework was synthesized from low cost and moisture-stable precursors, silatrane and titanium glycolate, under microwave instrument. The effect of the compositions (TPA^+ , NaOH and H_2O) and conditions (aging time, reaction time and reaction temperature) were studied. The suitable condition for synthesizing TS-1 was Si:0.1Ti:0.4NaOH:0.3TPA:114 H_2O at aging time 110h, reaction time 15h and

reaction temperature 150°C. The Si:Ti molar ratio 100.00-5.00 was studied and the results from XRD, FT-IR, SEM and DR-UV indicated that from this route highly crystalline and the Ti atoms are occupying in the zeolite framework. The reaction times were varied at different Ti loaded, which at higher titanium loading the higher reaction time was an important factor. The photocatalytic decomposition of 4-NP was used to test the activity of prepared TS-1 samples. The samples showed high efficiency in PCD of 4-NP and the PCD increased with amount of titanium loading.

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Table 6.1 The TS-1 samples at varies Si:Ti molar ratios and reaction time (h)

Sample	Si/Ti molar ratio	Reaction time (h)
a	100.00	15
b	33.33	15
c	20.00	20
d	14.29	25
e	10.00	25
f	7.69	35
g	5.88	35
h	5.00	35

Table 6.2 The photocatalytic degradation of 4-nitrophenol

Si/Ti (molar ratio)	Time for completely photocatalytic decomposition of 4-NP (h)
100.00	4.00
14.29	2.00
7.69	1.30
5.00	1.00

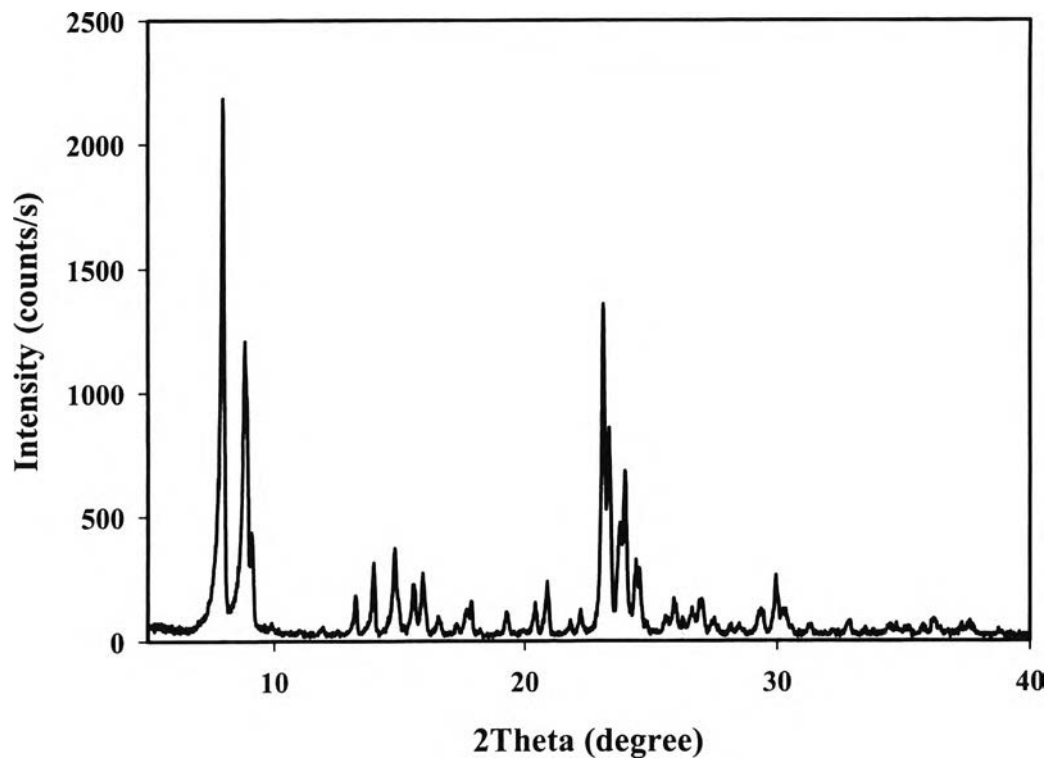


Figure 6.1 The XRD pattern of calcined TS-1 sample.

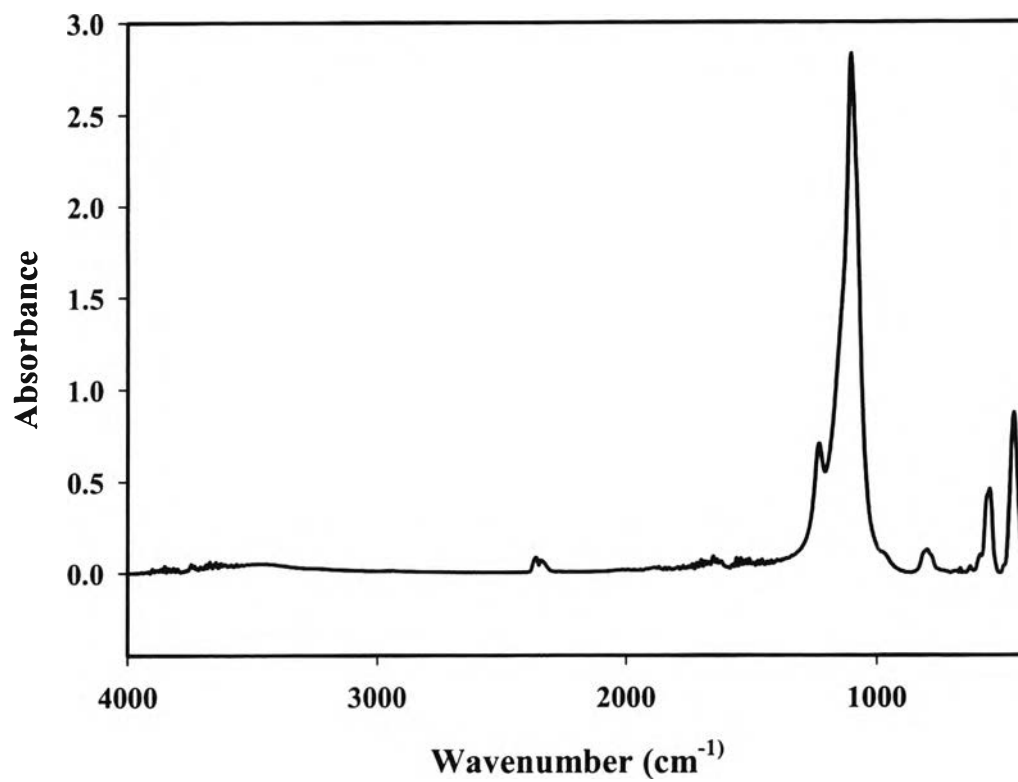


Figure 6.2 The FT-IR spectra of calcined TS-1 sample.

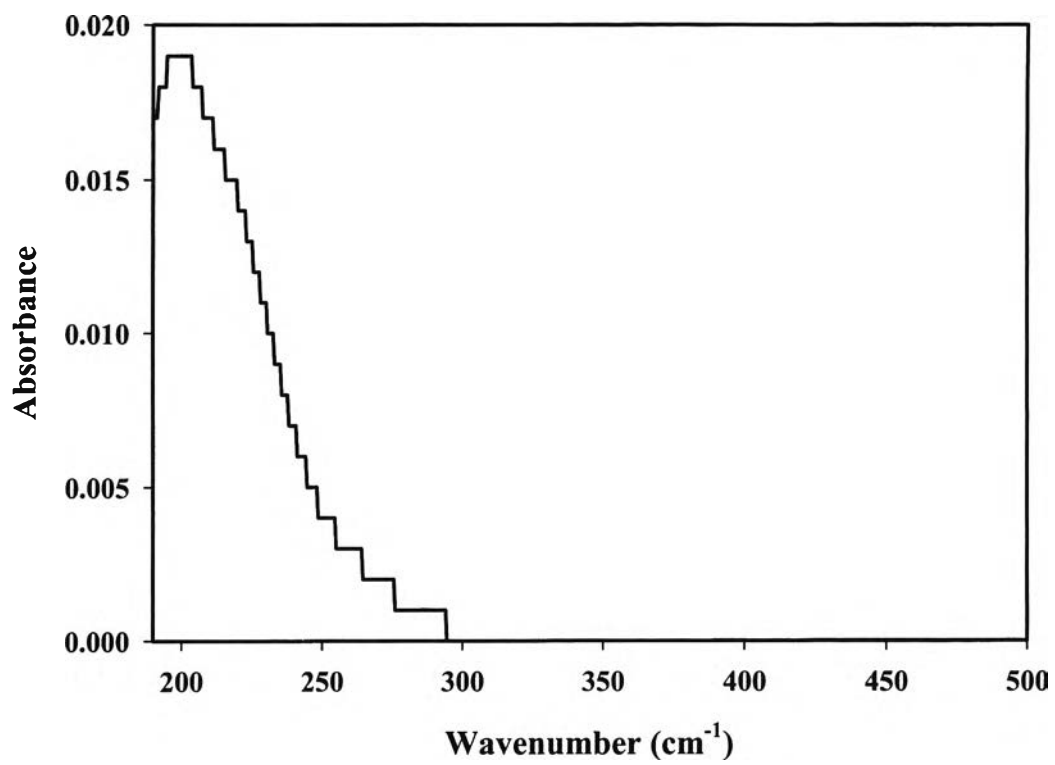


Figure 6.3 The DR-UV spectra of calcined TS-1 sample.

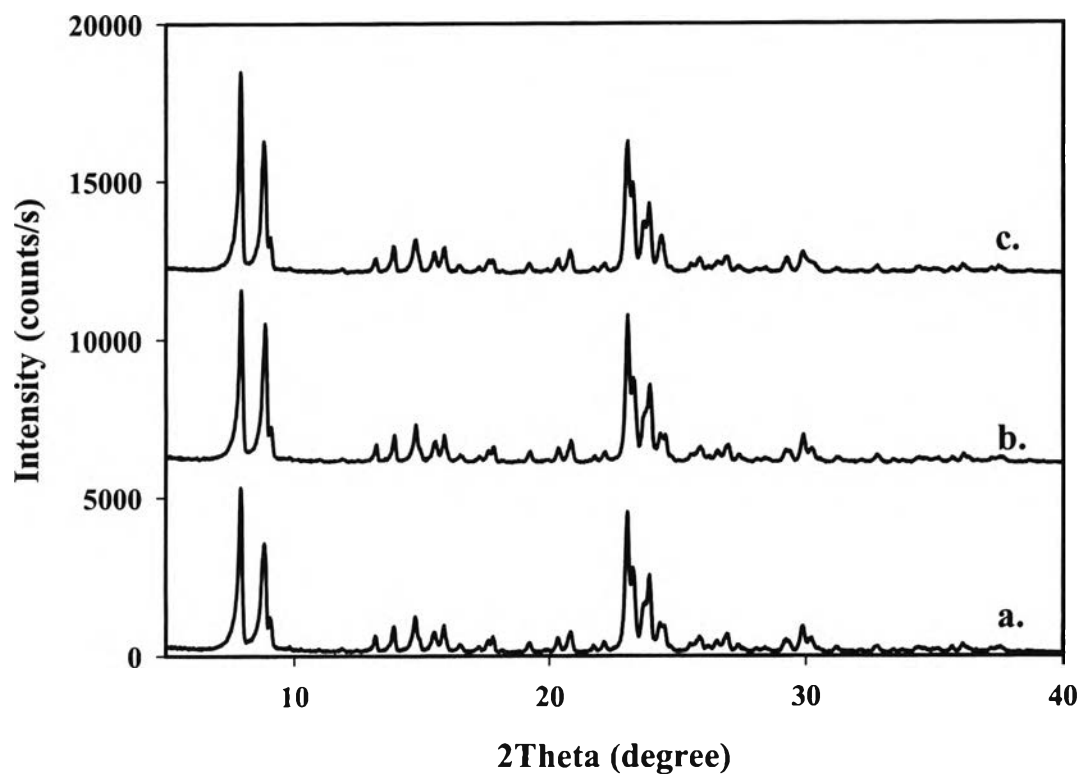


Figure 6.4 The XRD pattern of TS-1 samples at varies reaction temperature
a.) 120°C, b.) 150°C and c.) 170°C.

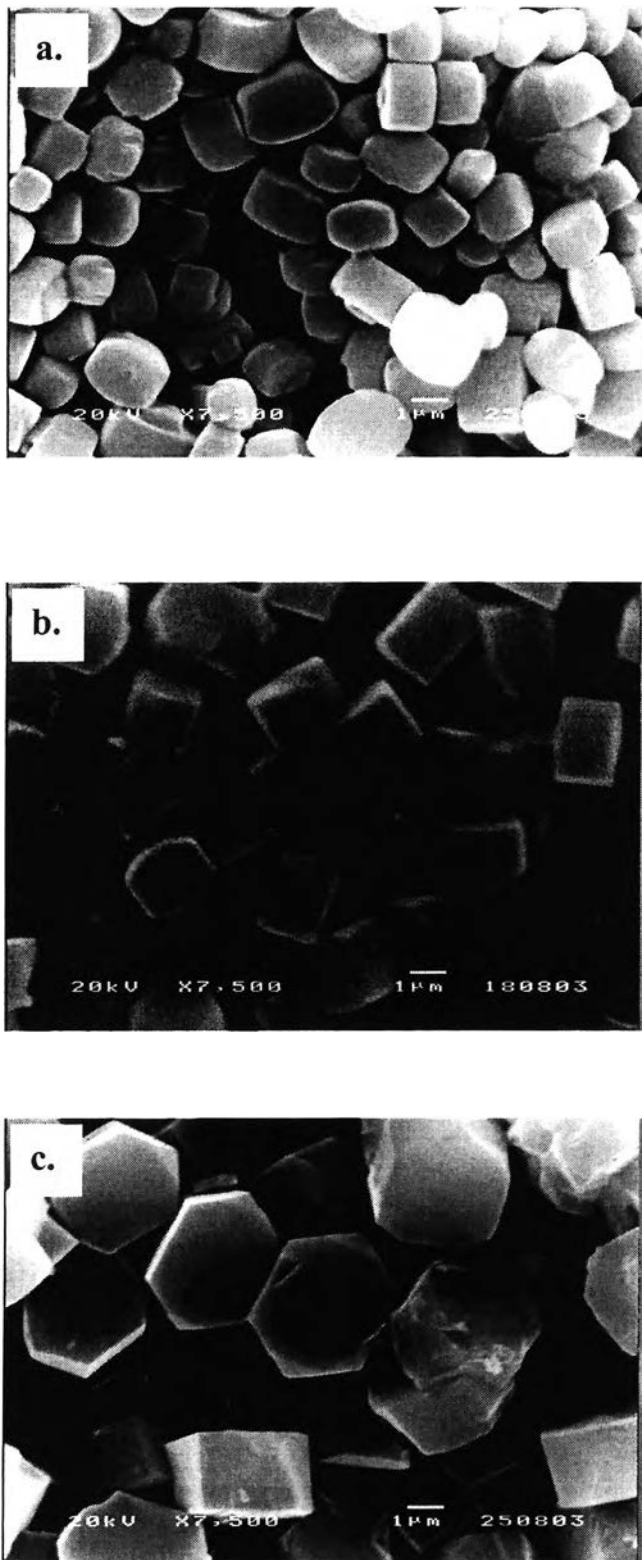


Figure 6.5 The SEM micrograph of TS-1 sample at varies reaction temperature a.) 120°C, b.) 150°C and c.) 170°C.

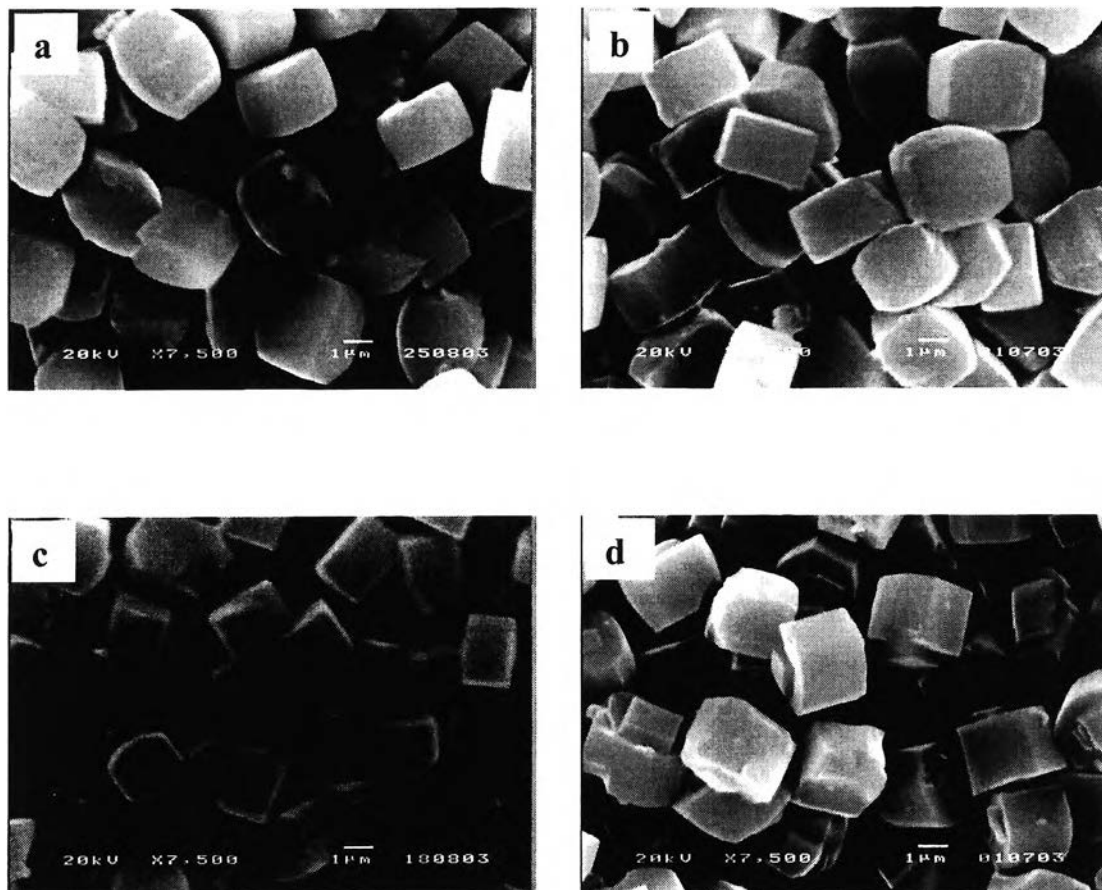


Figure 6.6 The SEM micrograph of TS-1 samples at varies reaction time a.) 5h, b.) 10h, c.) 15h and d.) 20h.

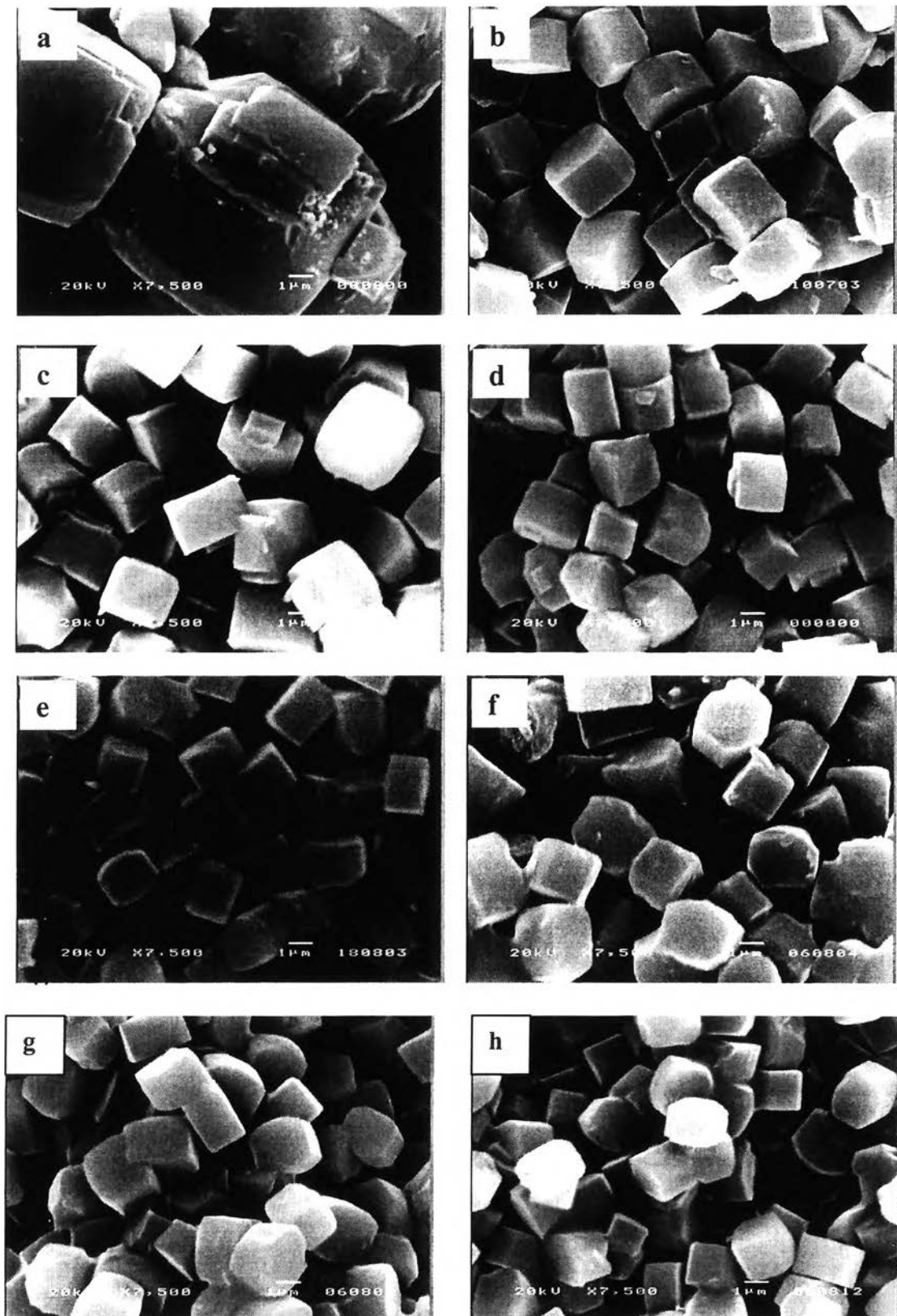


Figure 6.7 The SEM micrograph of TS-1 samples at varies aging time a.) 20h, b.) 60h, c.) 70h, d.) 90h, e.) 110h, f.) 130h, g.) 150h and h.) 170h.

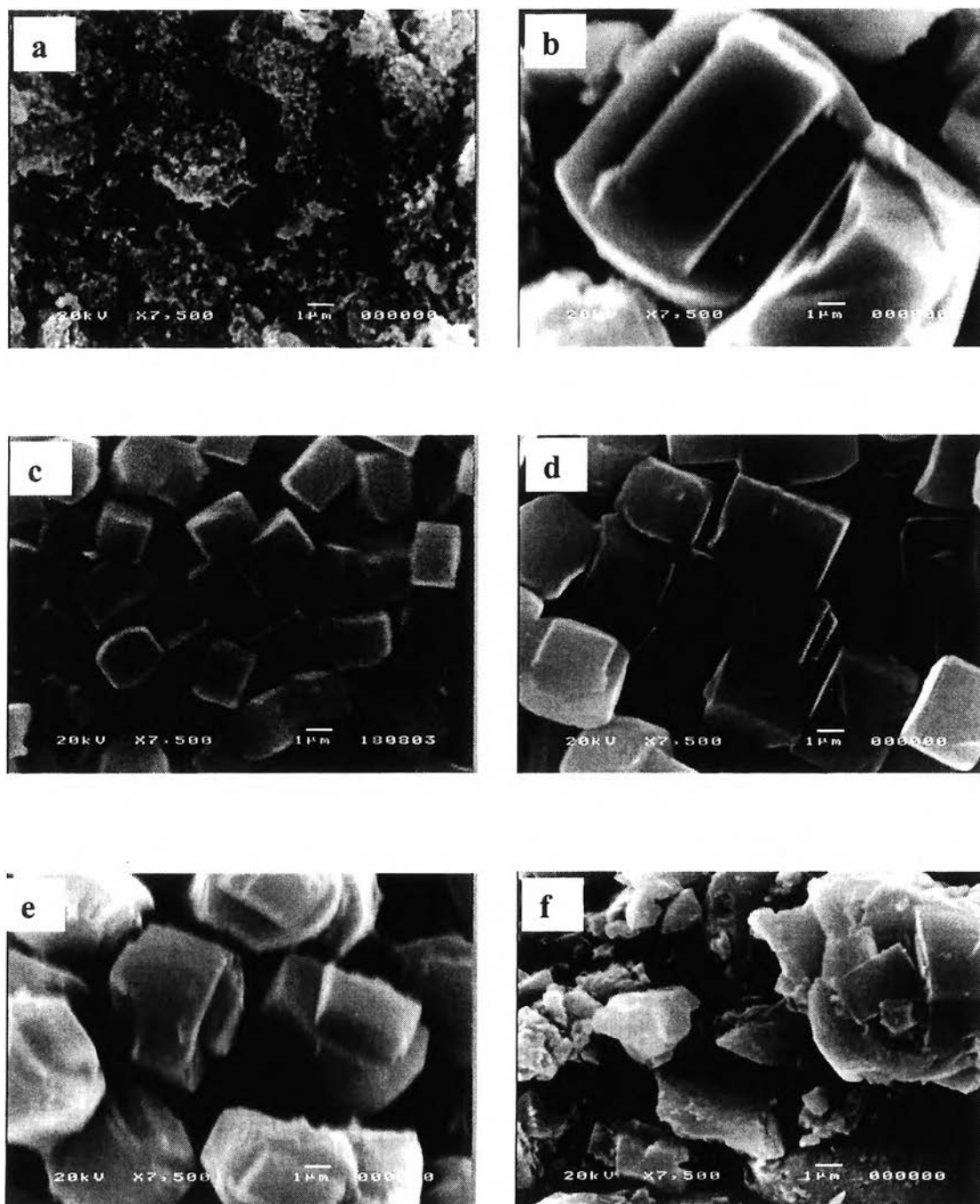


Figure 6.8 The SEM micrograph of TS-1 samples at varies NaOH:Si molar ratios a.) 0.1, b.) 0.3, c.)0.4, d.) 0.5, e.) 0.7 and f.) 1.0.

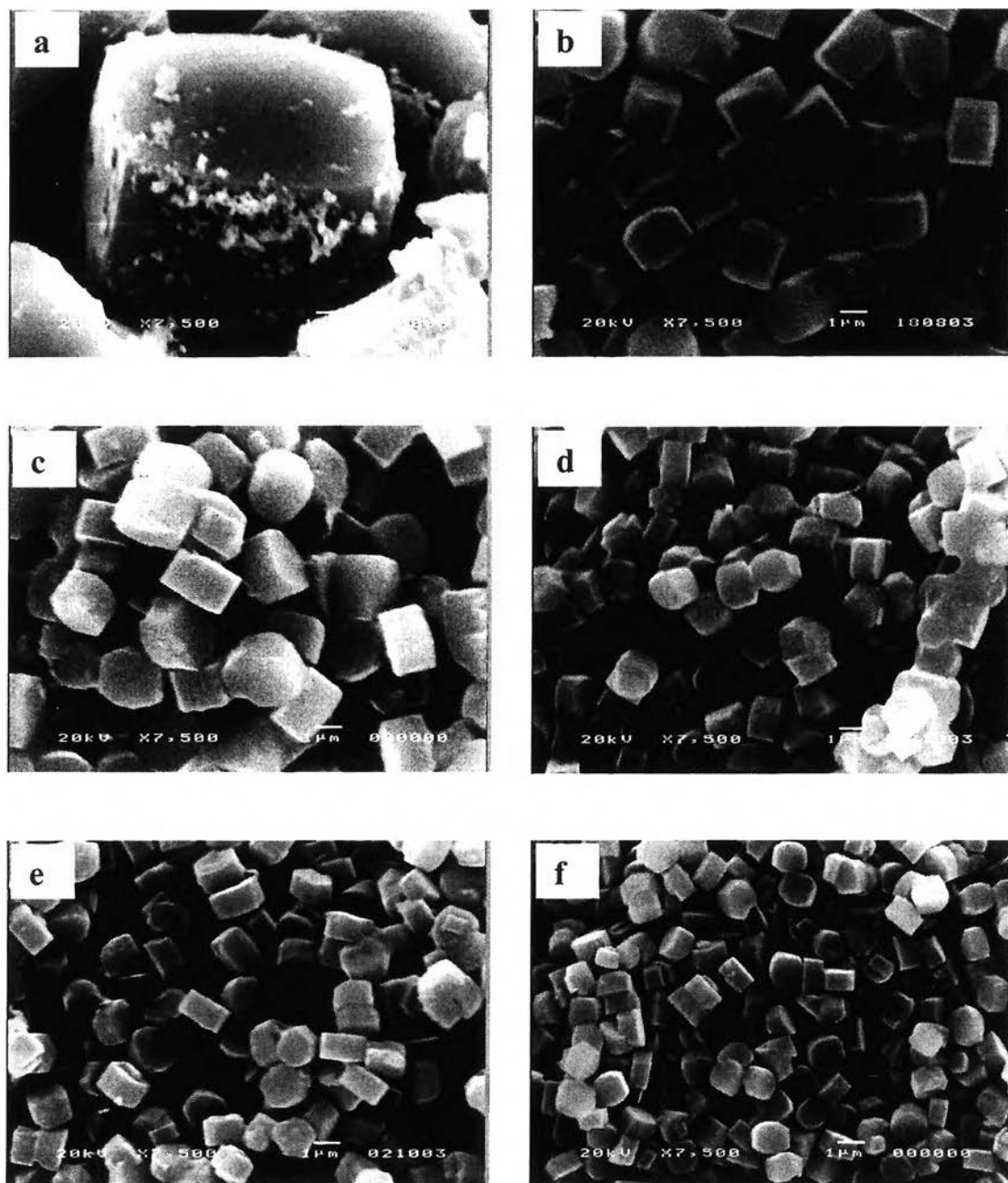


Figure 6.9 The SEM micrograph of TS-1 samples at varies TPA:Si molar ratios a.) 0.05, b.) 0.1, c.) 0.2, d.) 0.3, e.) 0.4 and f.) 0.5.

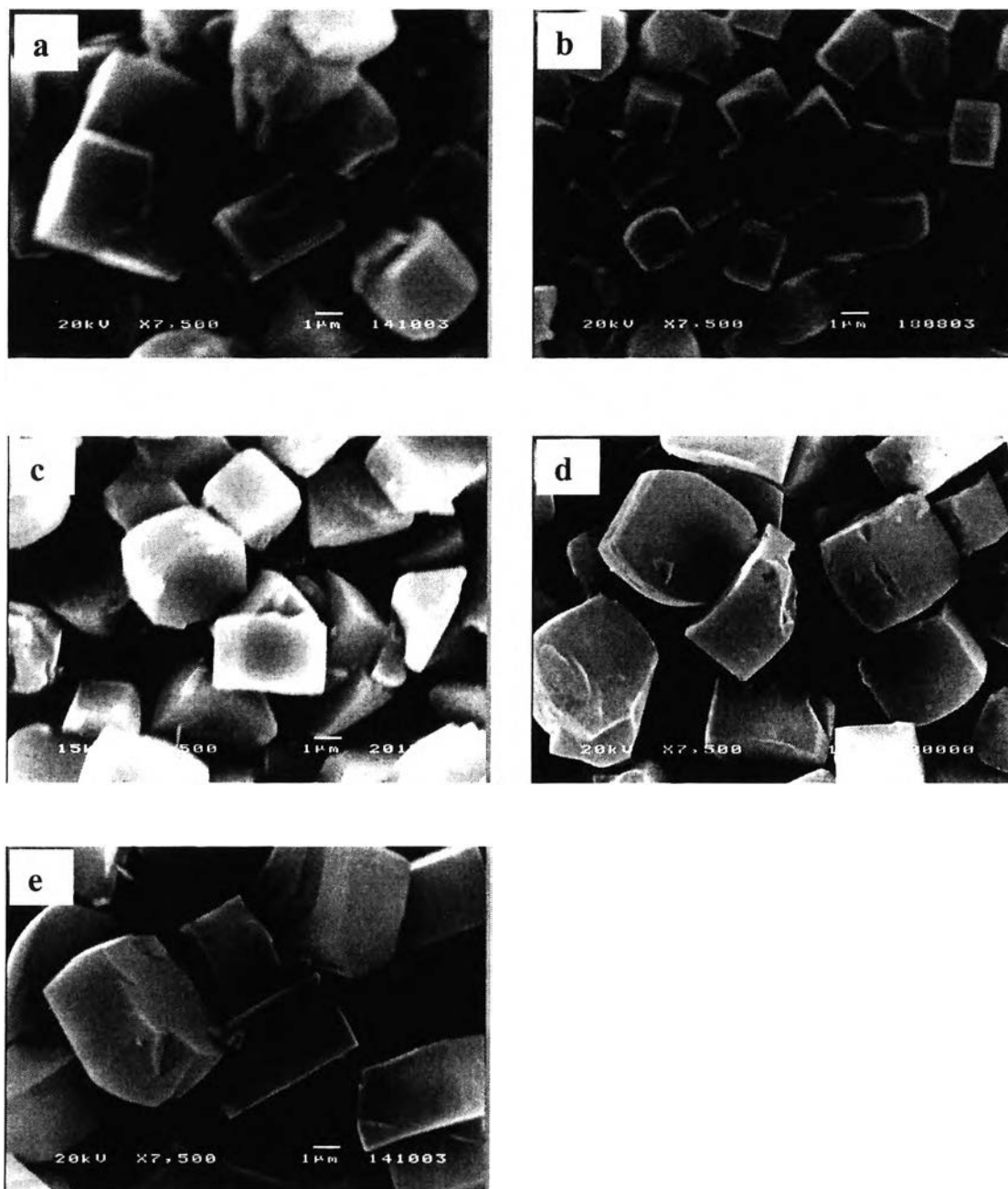


Figure 6.10 The SEM micrograph of TS-1 samples at varies H₂O:Si molar ratios a.) 80, b.) 114, c.) 140, d.) 170 and e.) 200.

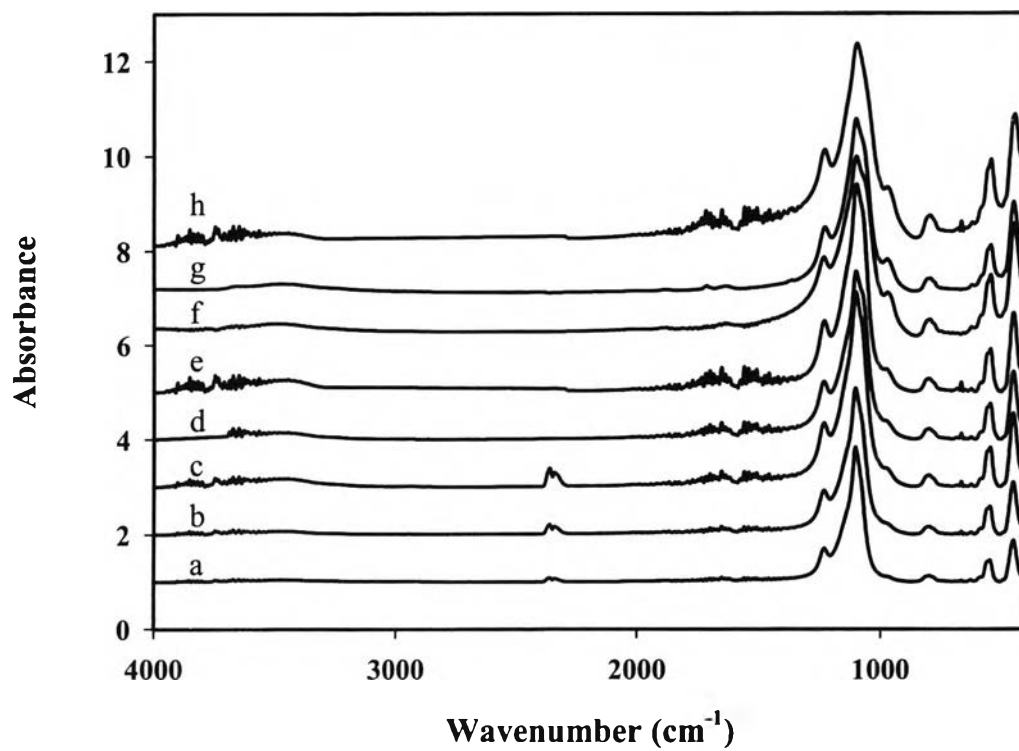


Figure 6.11 The FT-IR spectra of TS-1 sample at varies Si:Ti molar ratios a.) 100.00, b.) 33.33, c.) 20.00, d.) 14.29, e.) 10.00, f.) 7.69, g.) 5.88 and h.) 5.00.

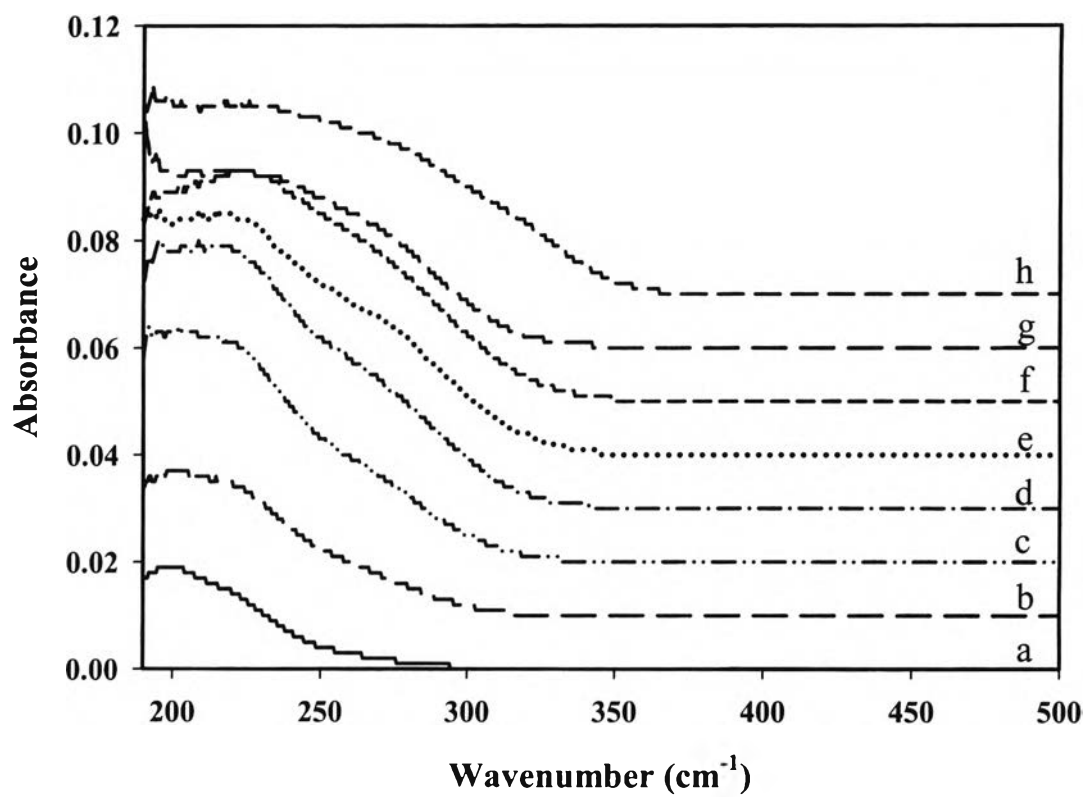


Figure 6.12 The DR-UV spectra of TS-1 sample at varies Si:Ti molar ratios a.) 100.00, b.) 33.33, c.) 20.00, d.) 14.29, e.) 10.00, f.) 7.69, g.) 5.88 and h.) 5.00.

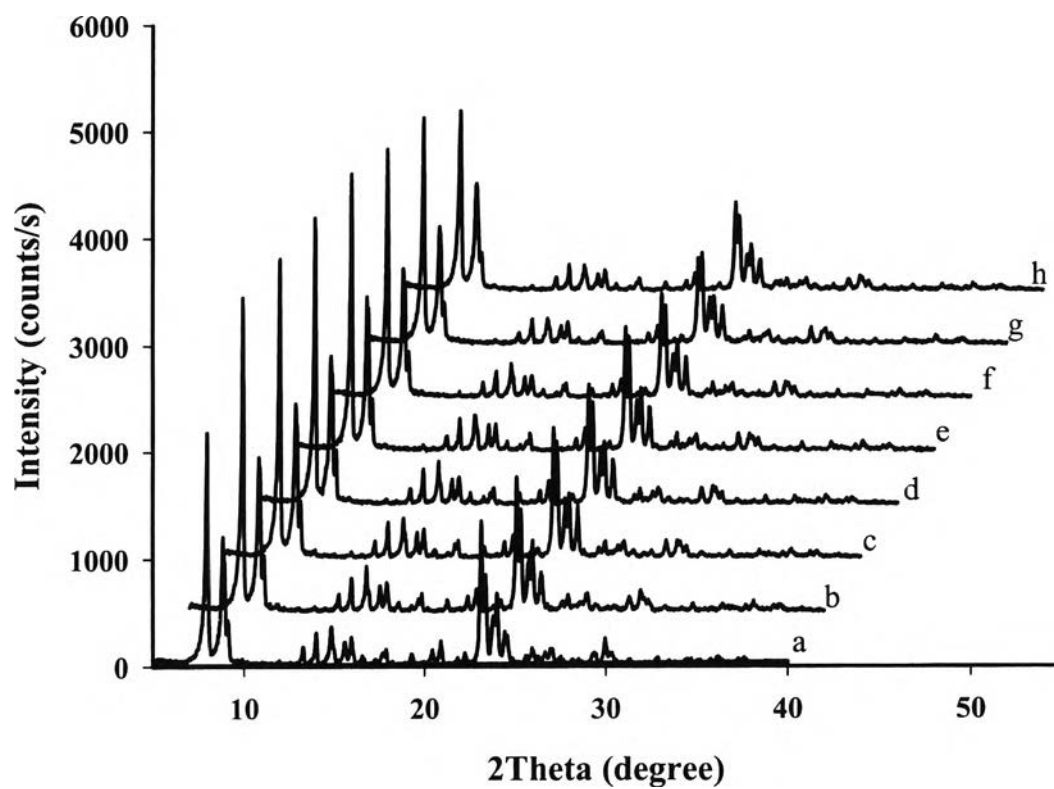


Figure 6.13 The XRD pattern of TS-1 sample at varies Si:Ti molar ratios a.) 100.00, b.) 33.33, c.) 20.00, d.) 14.29, e.) 10.00, f.) 7.69, g.) 5.88 and h.) 5.00.

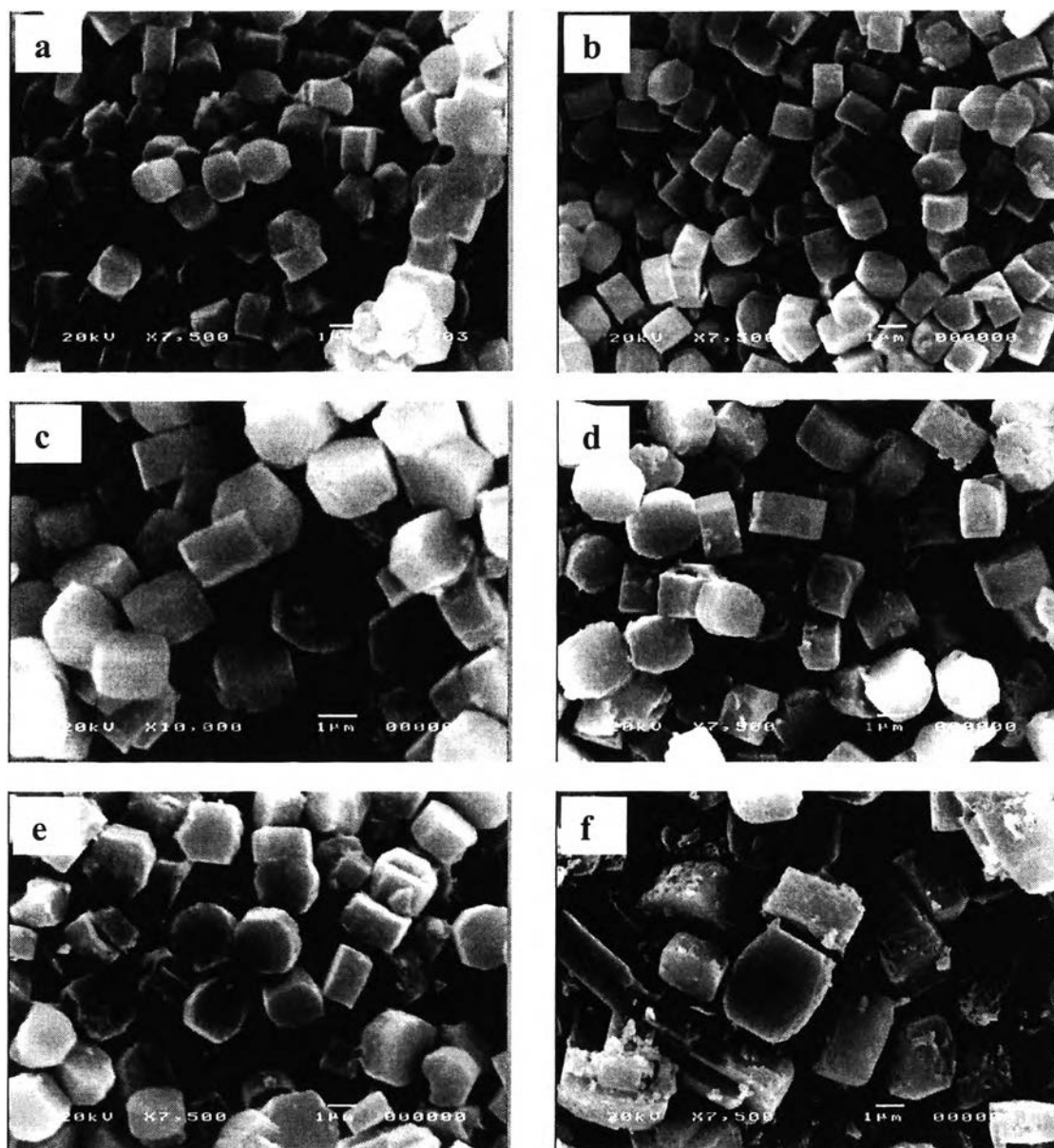


Figure 6.14 The SEM micrograph of TS-1 sample at varies Si:Ti molar ratios a.) 100.00, b.) 33.33, c.) 20.00, d.) 14.29, e.) 10.00, f.) 7.69, g.) 5.88 and h.) 5.00.