

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are classified into five major parts. Firstly, characteristic of metallosilicate structure by XRD of H-Al-Silicate or H(Al)ZSM-5, H-Fe-Silicate, H-Zn-Silicate, H-Ga-Silicate and Silicalite were observed. In the second part, the study of crystallite size, chemical composition were analyzed by SEM, XRF respectively and also discussed the result of qualitative analysis of ^{29}Si structure and ^{27}Al structure in framework by ^{29}Si MAS NMR and ^{27}Al MSA NMR, respectively. In the third part, the study effects of hydrothermal treatment of the catalysts on crystallinity. In the fourth part, we also discussed the result of the study of FT-IR to illustrate the species of metallosilicates. Finally, this research was completely explained by FT-Raman Spectroscopy.

5.1 Characterization of metallosilicate structure by XRD

X-ray diffraction (XRD) patterns for samples H-Al-Silicate [H(Al)ZSM-5], H-Fe-Silicate, H-Zn-Silicate, H-Ga-Silicate and Silicalite are displayed in Fig 5.1. The catalysts used in this part were synthesis to overview the difference of their characteristics and compare with H(Al)ZSM-5. The XRD patterns of all catalysts prepared in this laboratory by rapid crystallization method [71, 72] as direct synthesis, were similar to that of H(Al)ZSM-5, indicating that these metallosilicates have an MFI structure (i.e metallosilicates with ZSM-5 type structure) [65]. Metallosilicate with a ZSM-5 structure having metal M as a component will be denoted [M-ZSM-5] substituting for Al^{+3} position into framework [66].

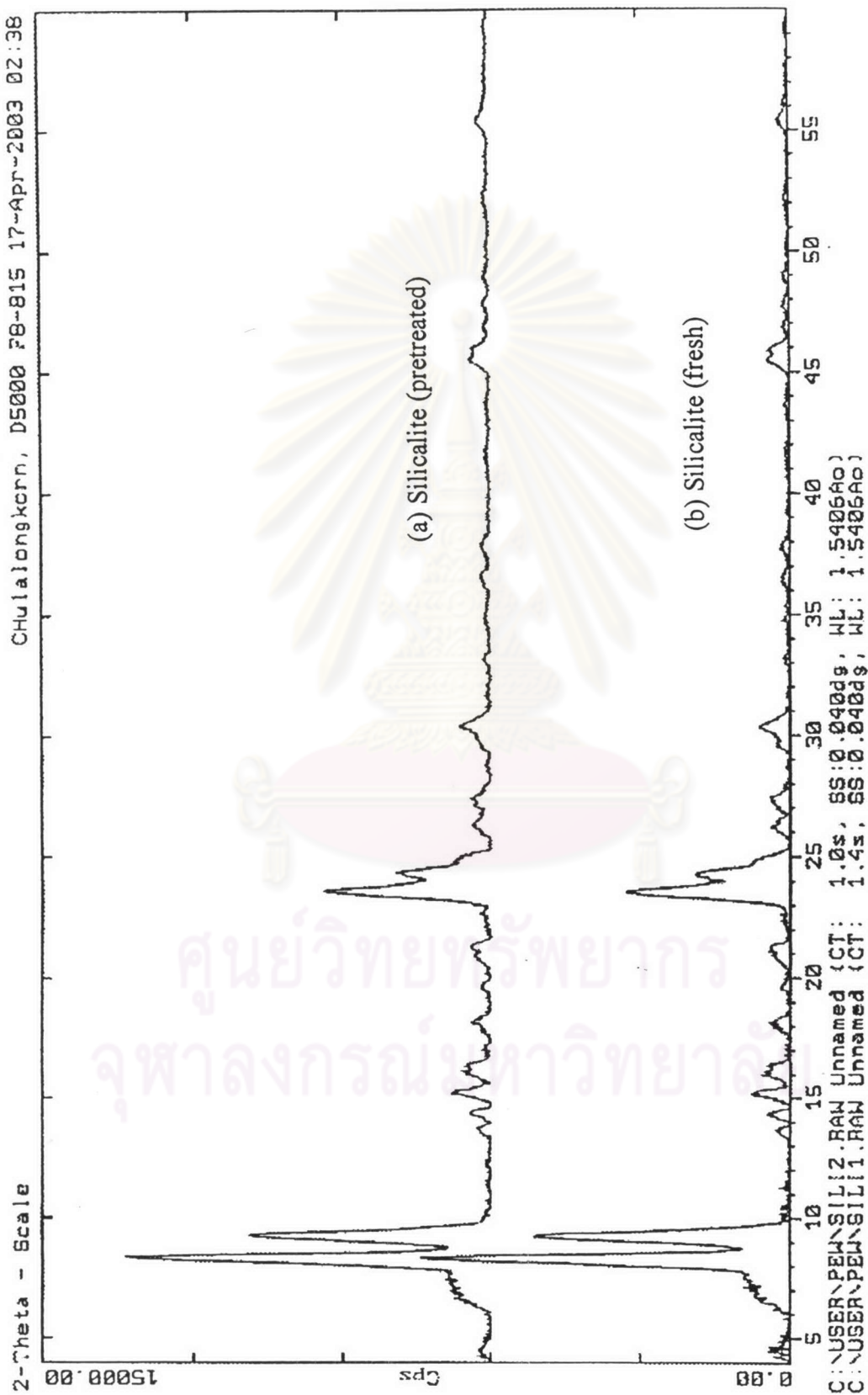


Figure 5.1 XRD patterns for catalysts

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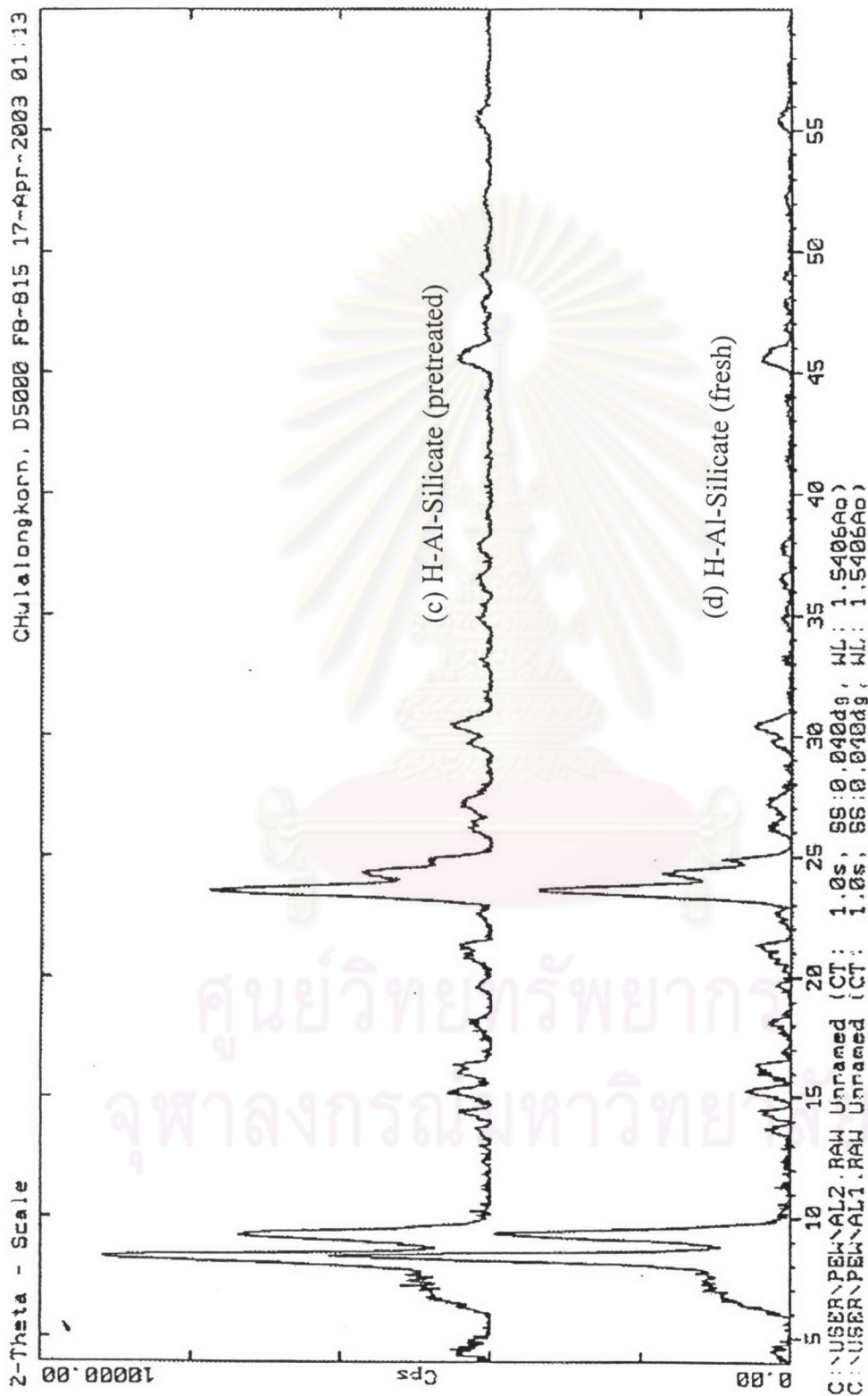


Figure 5.1 XRD patterns for catalysts (continued)

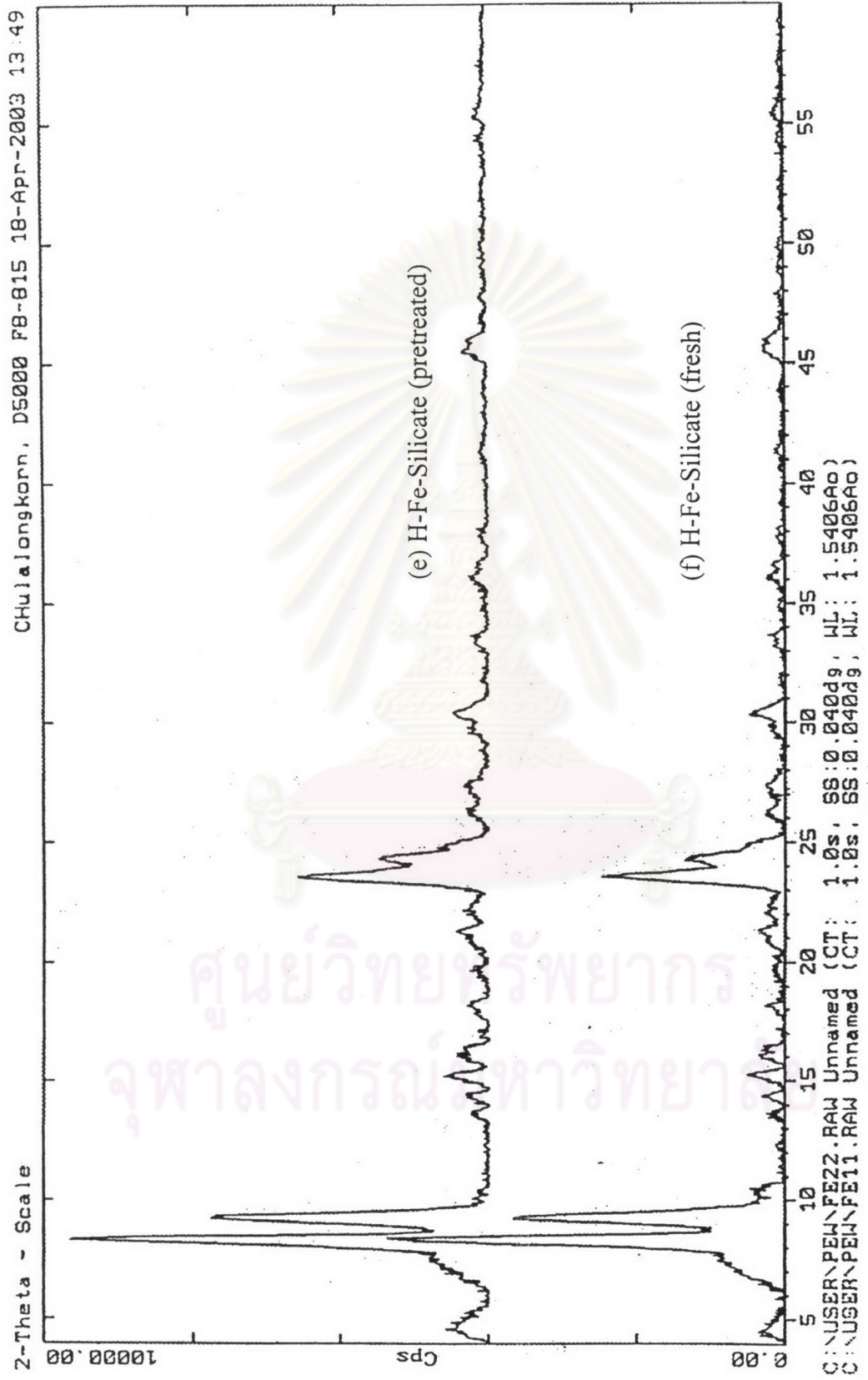


Figure 5.1 XRD patterns for catalysts (continued)



Figure 5.1 XRD patterns for catalysts (continued)

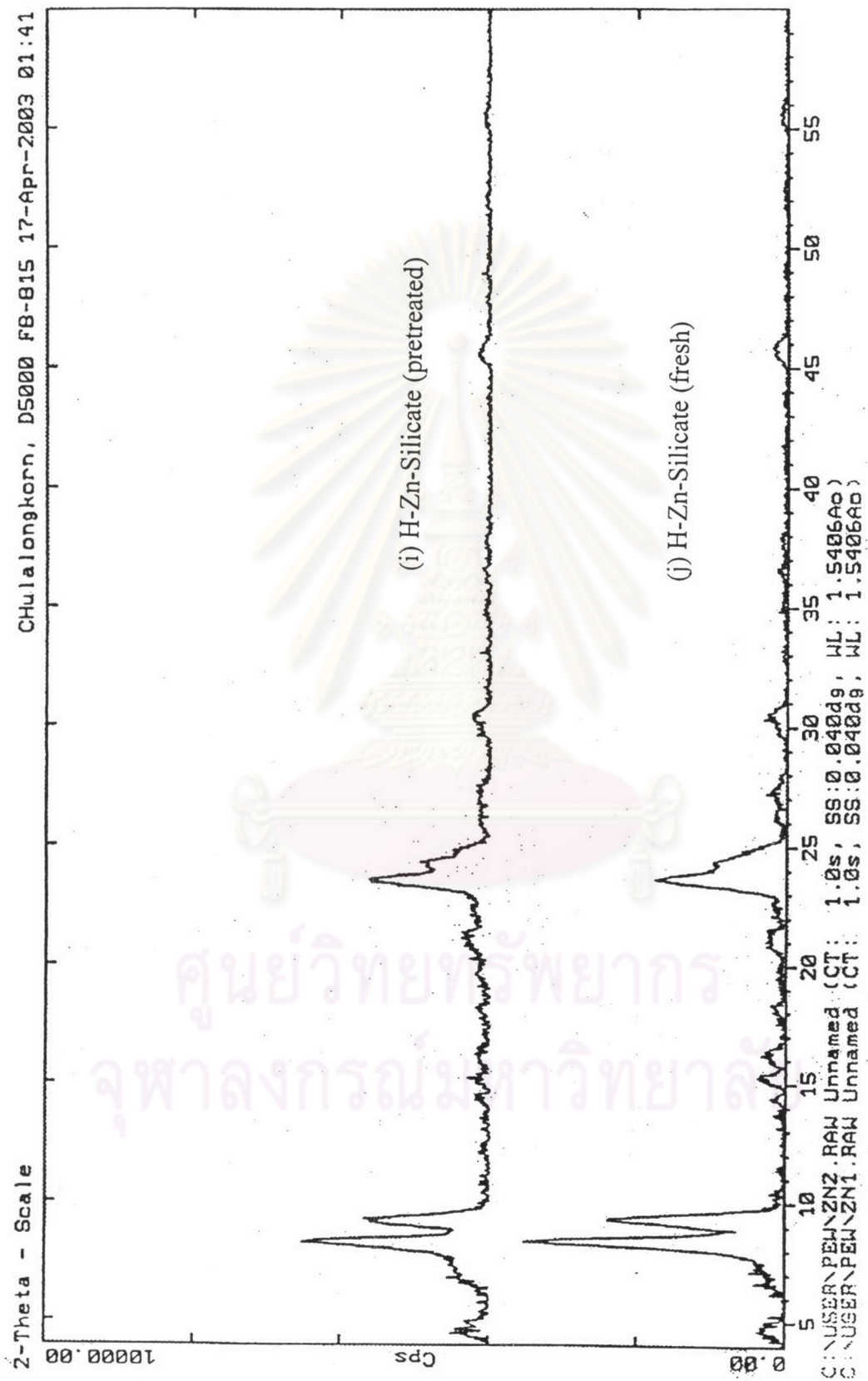


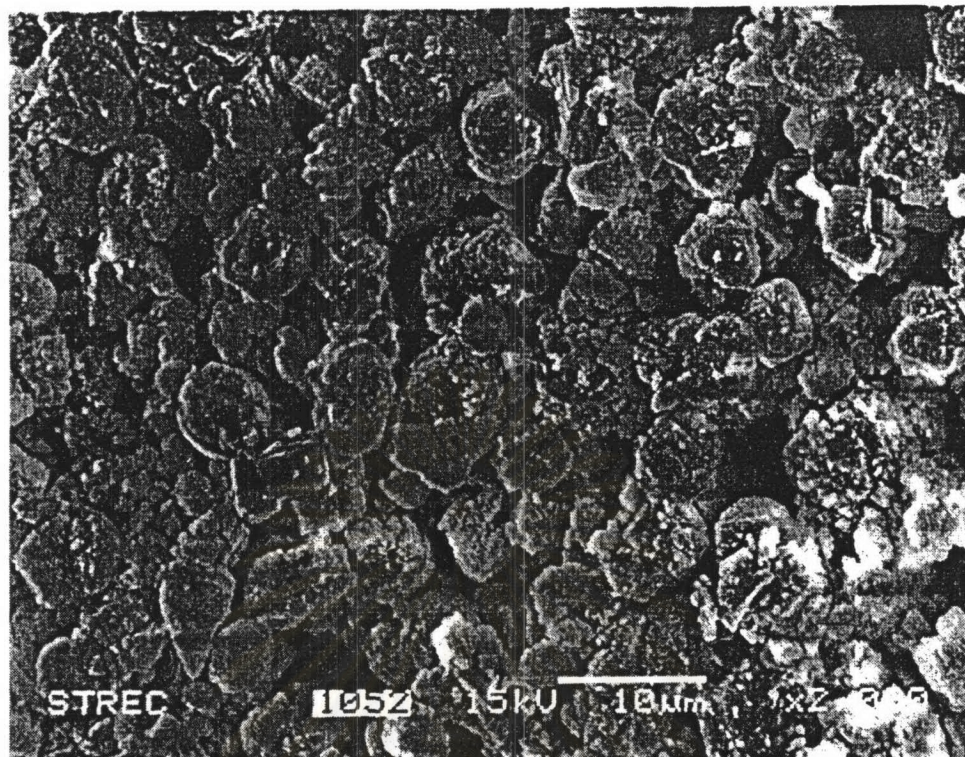
Figure 5.1 XRD patterns for catalysts (continued)

Moreover, The ZSM-5 structure can easily crystallize in pure silica form (silicalite) which could form as metallosilicate reaction mixture, giving the characteristic X-ray diffraction pattern without incorporating the desired metal component into the structure. However from the comparison of XRD patterns between the fresh and pretreated catalysts. We found that after pretreatment, all catalysts still maintain metallosilicate structure having MFI structure. This indicates that hydrothermal treatment does not affect to change the structure of metallosilicate catalysts. But, the intensity of X-ray diffraction lines of all catalysts after pretreatment are lower than that without pretreatment. It can be indicated that, after pretreatment, all catalysts have lower crystallinity causing the loss of stability from hydrothermal treatment.

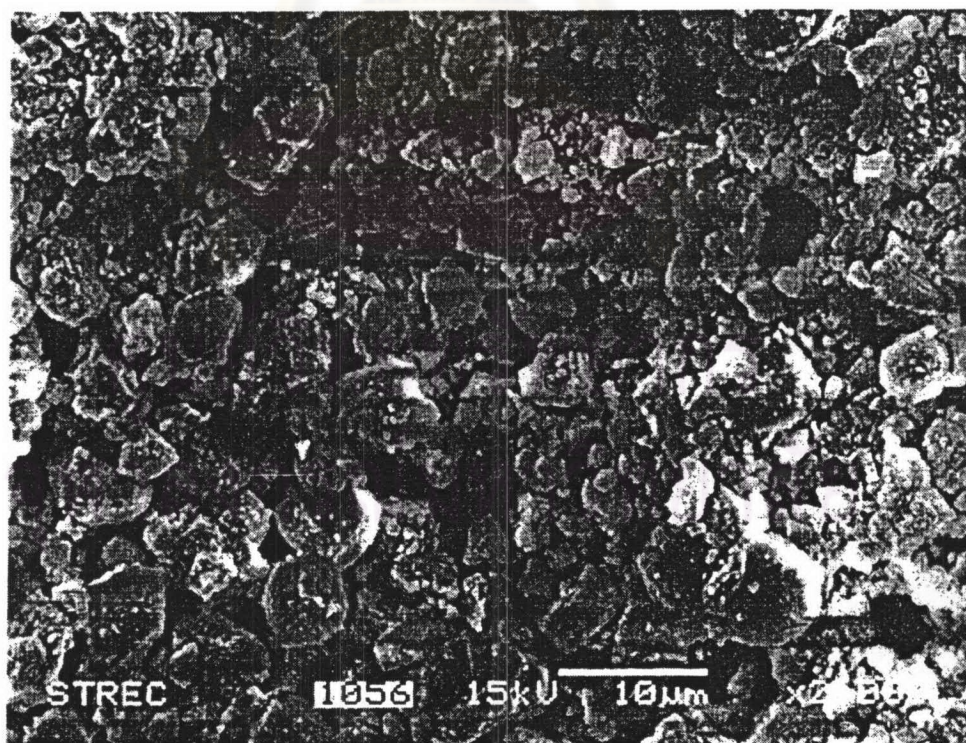
5.2 The study of crystallite size, chemical composition and ^{29}Si and ^{27}Al MAS NMR structure in framework of catalysts

5.2.1 Morphology

Scanning electron microscope photographs (SEM) of the catalysts are shown in Figure 5.2 that shown the zeolite and metallosilicate particles are not strongly isolated, but are agglomerations of smaller crystallites with having average crystal size diameter of 5.5, 5.5, 5.6, 5.7, 5.5, 5.5, 5.3, 5.3, 5.6, 5.6 μm . (from Fig 5.2 a to j) respectively and have a basically spherical habit with truncated and stepped faces. The conclusion reached from this data is that a large number of nuclei were formed in the initial stages of crystallization, causing growth of a large number of small, irregularly shaped crystallites. When compared crystallite size between

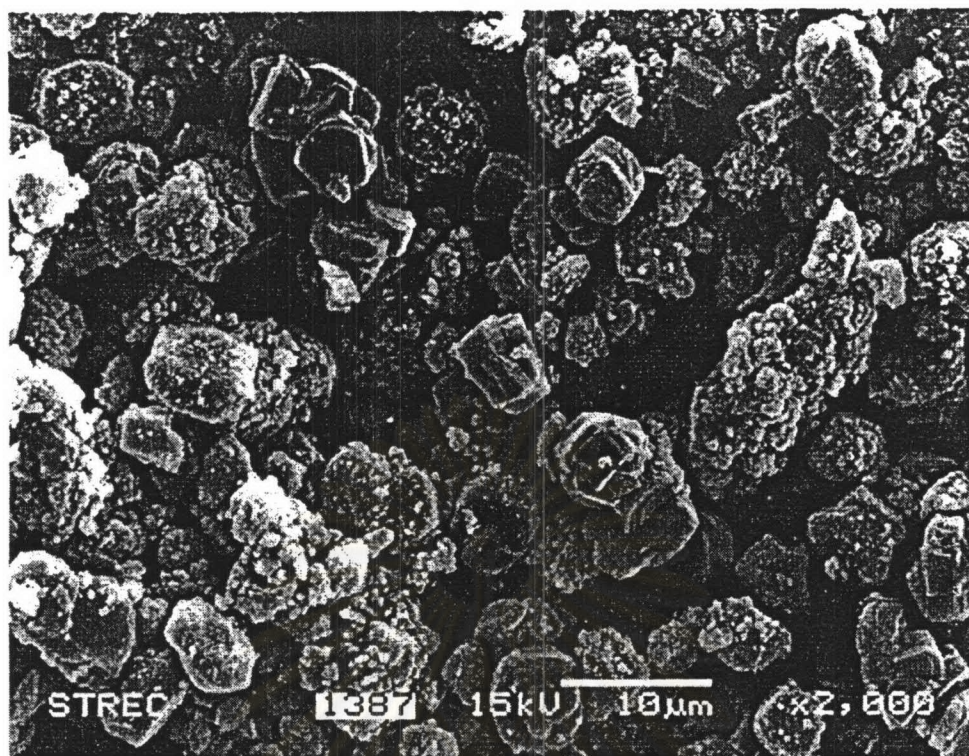


a) H-Fe-Silicate (fresh)

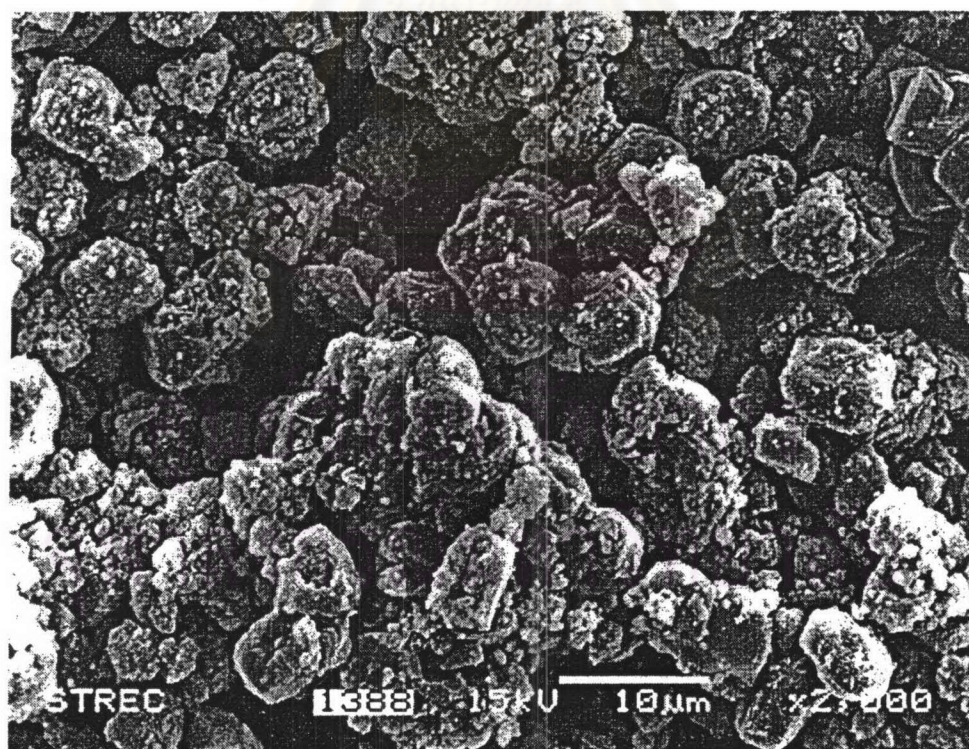


b) H-Fe-Silicate (pretreated)

Figure 5.2 SEM Photographs of the catalysts

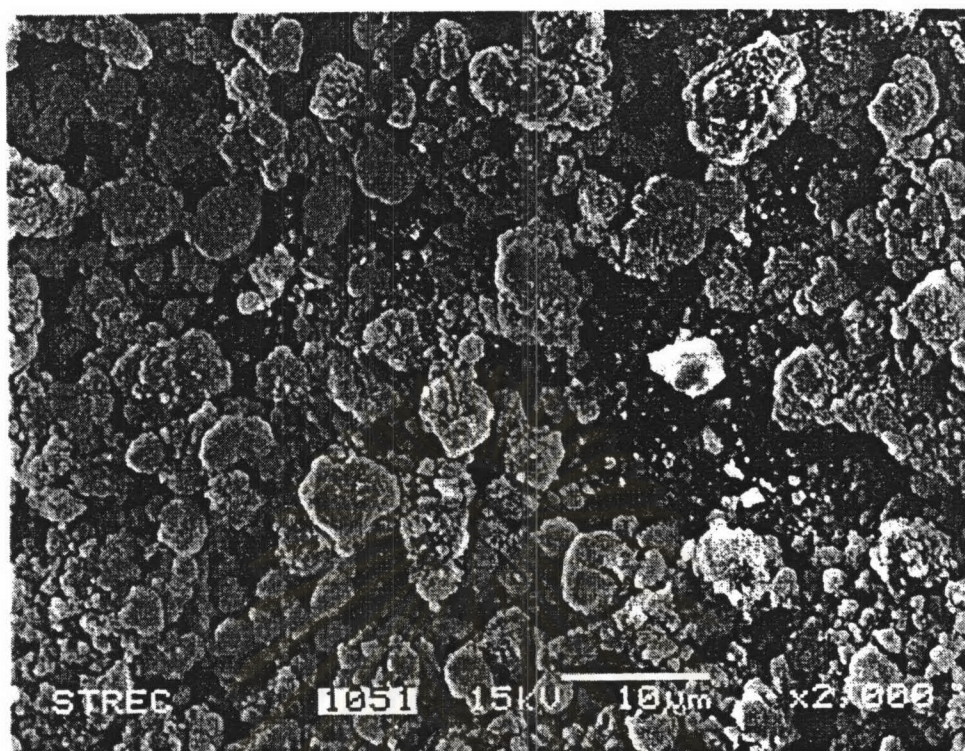


c) H-Ga-Silicate (fresh)

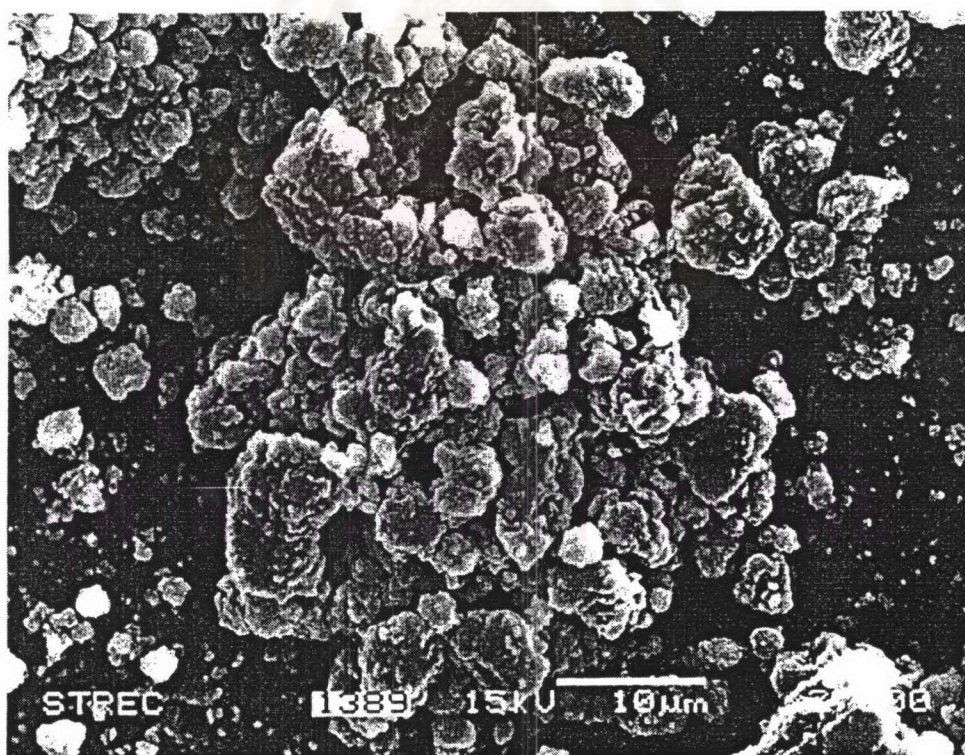


d) H-Ga-Silicate (pretreated)

Figure 5.2 SEM Photographs of the catalysts (continued)

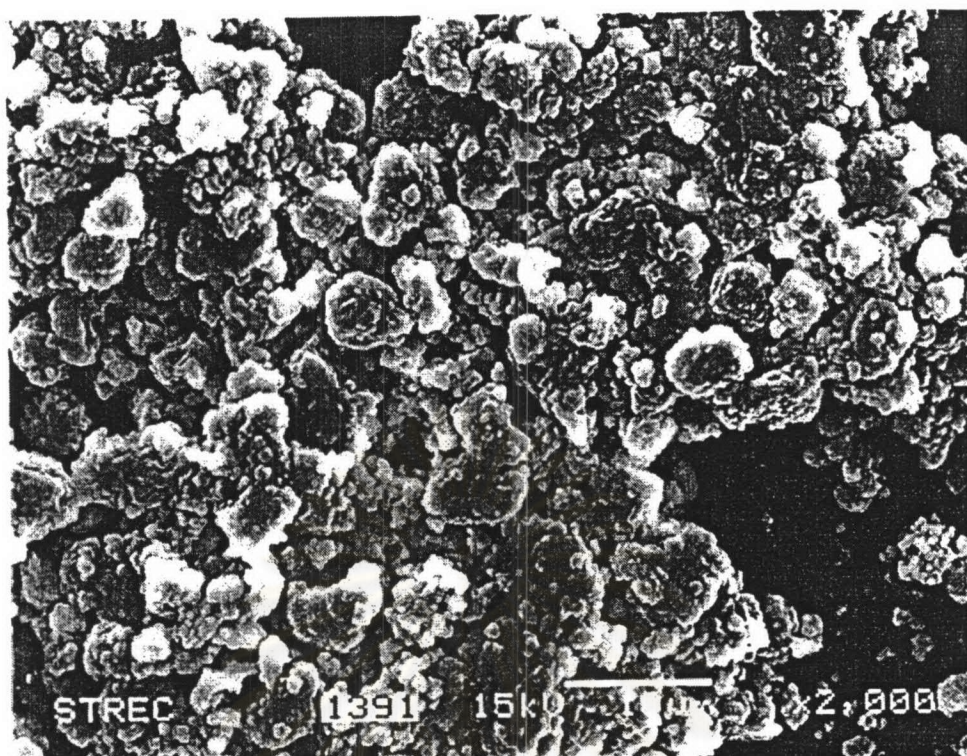


e) H-Zn-Silicate (fresh)

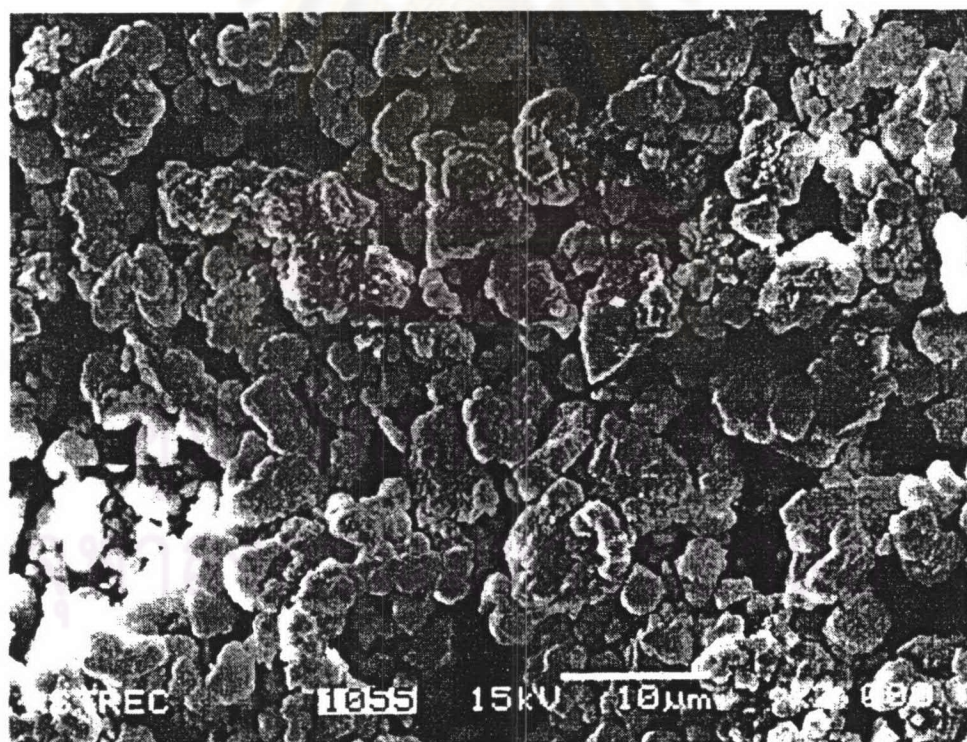


f) H-Zn-Silicate (pretreated)

Figure 5.2 SEM Photographs of the catalysts (continued)

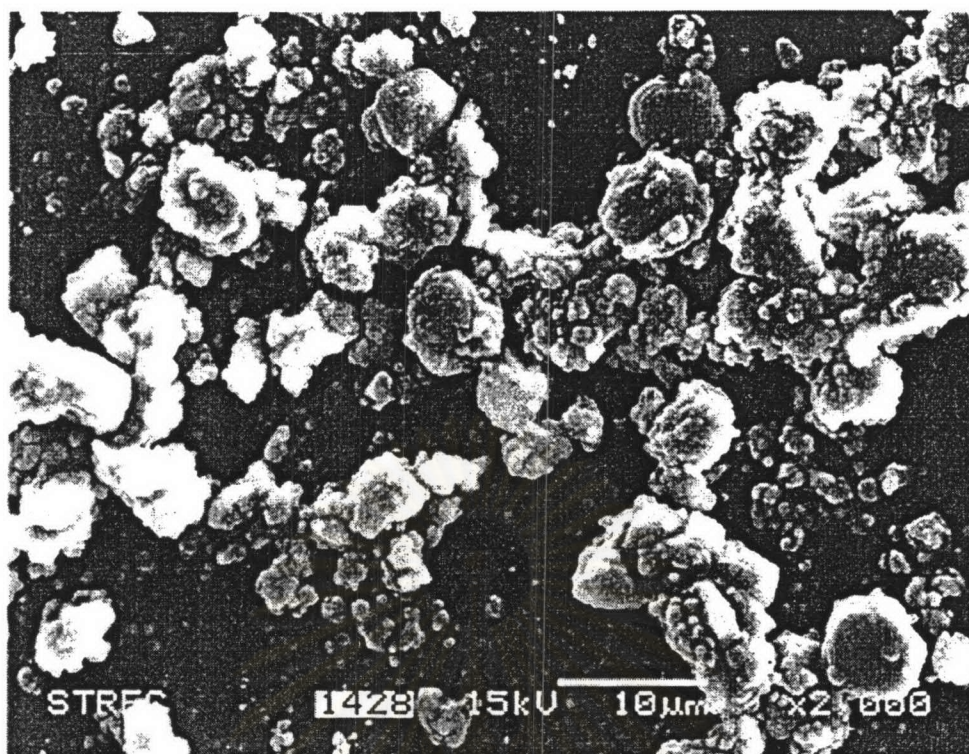


g) H-Al-Silicate (fresh)

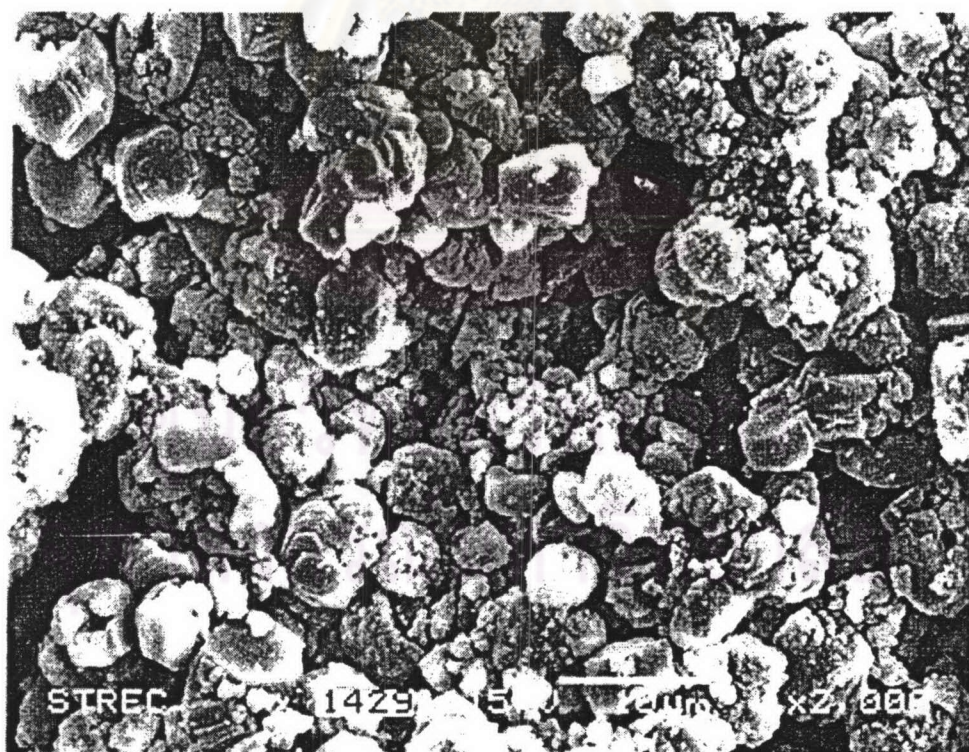


h) H-Al-Silicate (pretreated)

Figure 5.2 SEM Photographs of the catalysts (continued)



i) Silicalite (fresh)



j) Silicalite (pretreated)

Figure 5.2 SEM Photographs of the catalysts (continued)

before and after hydrothermal treatment; particle size do not change and similarly particle size of all catalyst both before and after hydrothermal treatment. Moreover, It was found that morphology of catalyst both fresh and pretreated catalyst have similar morphology. No change of structure was observed in hydrothermal treatment at 600°C in 10 mole% water for 24 hr. This indicates that the hydrothermal treatment condition does not affect to morphology and particle size of catalysts.

5.2.2 Chemical composition and ^{29}Si and ^{27}Al MAS NMR structure in framework of catalysts

The results of quantitative analysis of Si/Metal ratio in the synthesized crystallys are shown in Table 5.1 . The amount of metal present in the metallosilicates were determined by X-ray Fluorescence analysis (XRF)

The four metallosilicate catalysts show values of Si/Metal ratio with identical Si/Metal ratio in the original gel (predict) they have similar measured Si/Metal ratio (fresh) after crystallization. This indicates that it have metal incorporation into structure. A possible reason for this high amount of incorporation of metal in structure is the template synthesis of these materials with preparation the MFI structure the TPA^+ cation in either the hydroxide or bromide form as template has been the most successful and metallosilicate catalysts of high quality were obtained from preparation using TPABr [67]. However, from having highly amount of incorporation of metal in structure, it is suggested that in the case of metallosilicate, almost of all of Al, Fe, Ga and Zn can enter the structure of metallosilicate because of this is synthesis without addition other metal as second component in the zeolite synthesis hinders the incorporation of Fe, Ga and Zn into the structure as well as competition during the preparation of two components heteroatom-containing zeolite system. For Si/Metal ratio (pretreated), the content of metal loaded was not significantly changed by the pretreatment as seen from the XRF data. This indicated that there was no significant loss of metal species such as evaporation of metal due to the hydrothermal treatment.

Table 5.1 Zeolite and Metallosilicate synthesized and used in this work

Metallosilicate catalyst	Predict Si/Metal ^a	Measure		Strength of chemical bond ^b (kJ/mol)	%Crystallinity ^c (fresh)	% Crystallinity ^c (pretreated)	%Decreasing
		Si/Metal ^a (fresh)	Si/Metal ^a (pretreated)				
Silicalite	∞	∞	∞	Si-O = 799.6±13.4	100	95	5%
H-Al-Silicate	25	25.3	25.1	Al-O = 511±3	88	81	8%
H-Fe-Silicate	25	26.6	26.3	Fe-O = 390.4±17.2	73	66	10%
H-Ga-Silicate	25	23.5	23.2	Ga-O = 353.5±41.8	47	43	9%
H-Zn-Silicate	25	22.3	22.2	Zn-O = 159±4	45	38	15%

^aMetal = Al, Fe, Ga, Zn

^b = From Handbook of chemistry and Physics (David R Lide editor-in-chief 81st edition 2000-2001) p. 9-51 to 9-56

^c = compare with Silicalite (fresh)

For ^{29}Si MAS NMR spectra of silicalite, H-Al-Silicate, H-Fe-Silicate, H-Ga-Silicate and H-Zn-Silicate are shown in Fig 5.3. In the spectrum of silicalite the observed signal at -106 to -120 ppm can be attribute to Si(4Si) [68]. This is suggested that each of the Si site is coordinated to four oxygen atoms with tetrahedrally coordinate by oxygen atoms and it have attachment during Si-O bond. For H-Al-Silicate, Si (0Al) is at about -112 ppm and Si (3Si (1Al)) is at about -104 ppm [69]. This signal show that having substitution of Al atom by tetrahedral coordinate with oxygen. From ^{27}Al MAS NMR spectra of H-Al-Silicate is obtained by comparison of corresponding peak intensity of tetrahedral aluminum (55 ppm.) [79] Both ^{29}Si MAS NMR and ^{27}Al MAS NMR indicate that Al^{+3} cation can be incorporate into the tetrahedral zeolite framework site of molecular sieve structure during synthesis. For ^{29}Si MAS NMR spectra of H-Fe-Silicate, the observed signal at -104 ppm can not be attributed to Si (3Si (1Fe)). This indicate that Fe^{+3} may be incorporated into the tetrahedral zeolite framework site but can not be seen with ^{29}Si MAS NMR by must measure with EXAFS by Alexis T. Bell and et al. [85]. That, this apparatus have no in Thailand. It have only Si (0Fe) or Si (4Si) which is at about -113 ppm. For H-Ga-Silicate and H-Zn-Silicate; Si (0Ga or 0Zn) are at about -112 ppm and Si (3Si (1Ga)) or Si (3Si (1Zn)) are at about -104 ppm [69, 70]. These signals show that having substitution of Ga and Zn atom can be incorporate into the tetrahedral zeolite framework sites. From the about spectrum resonance of ^{29}Si NMR spectra of H-Al-Silicate, H-Ga-Silicate and H-Zn-Silicate; these signals show that having substitution of T atom by other tetrahedral coordinate element (Al, Ga, Zn, etc.) and metals cation can be incorporated into the tetrahedral zeolite framework sites of molecular sieve structure during synthesis. That means each of the zeolite site; Si atom is coordinated to oxygen atom and metal atom (Al, Ga, Zn) and these catalysts system have attachment during Metal-Oxygen boned to form O-metal-O-Si-O nuclei (the metal is Al, Ga, Zn) [73].

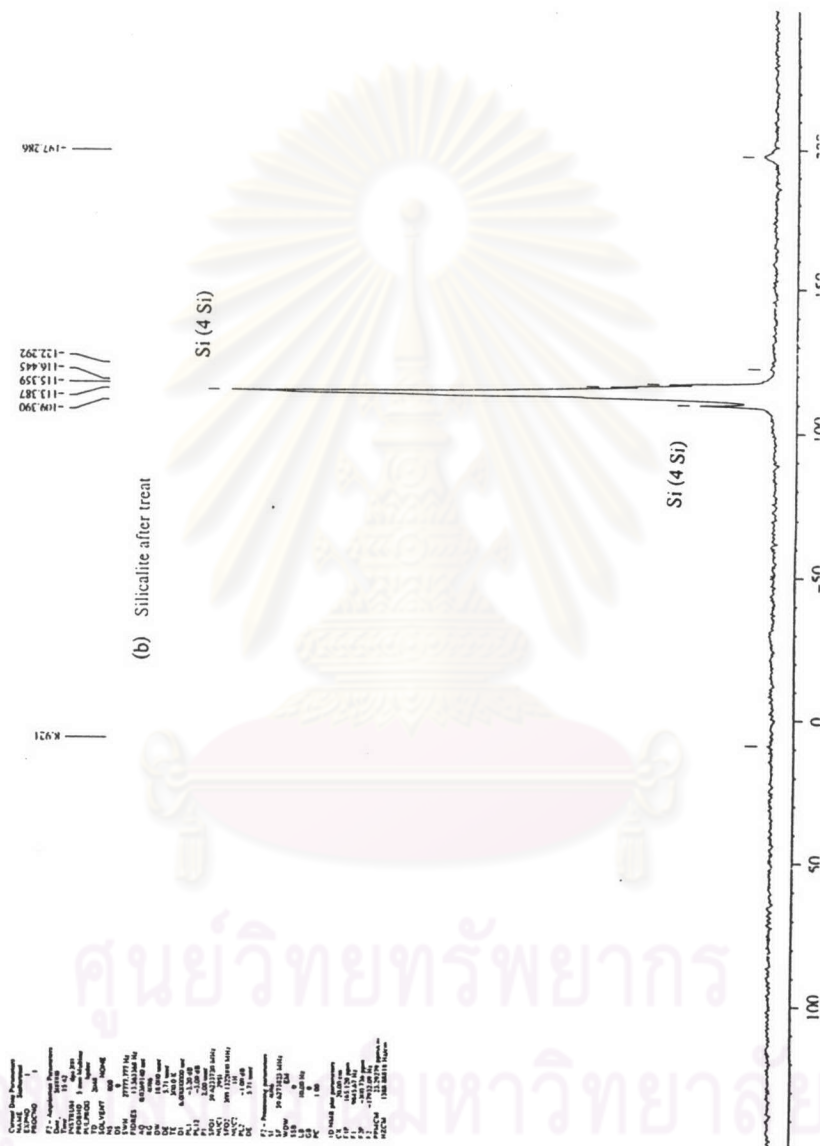
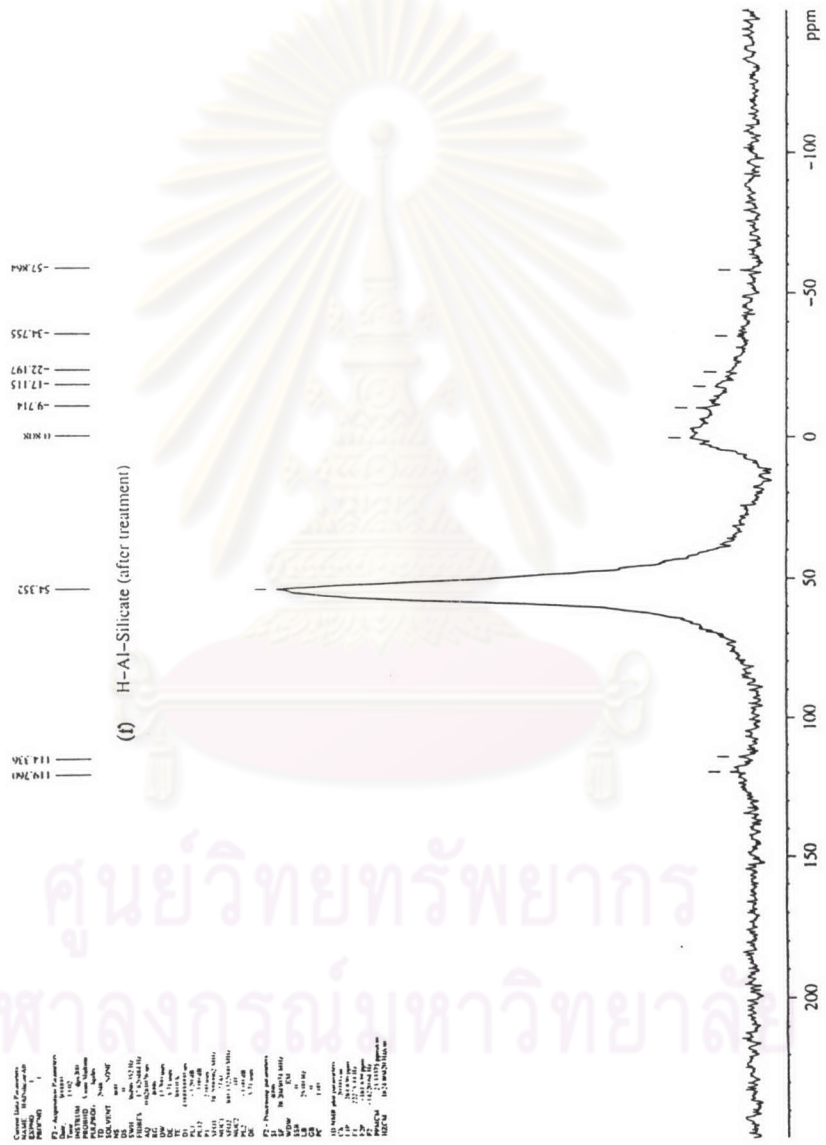


Figure 5.3 ²⁹Si NMR Spectra (continued)



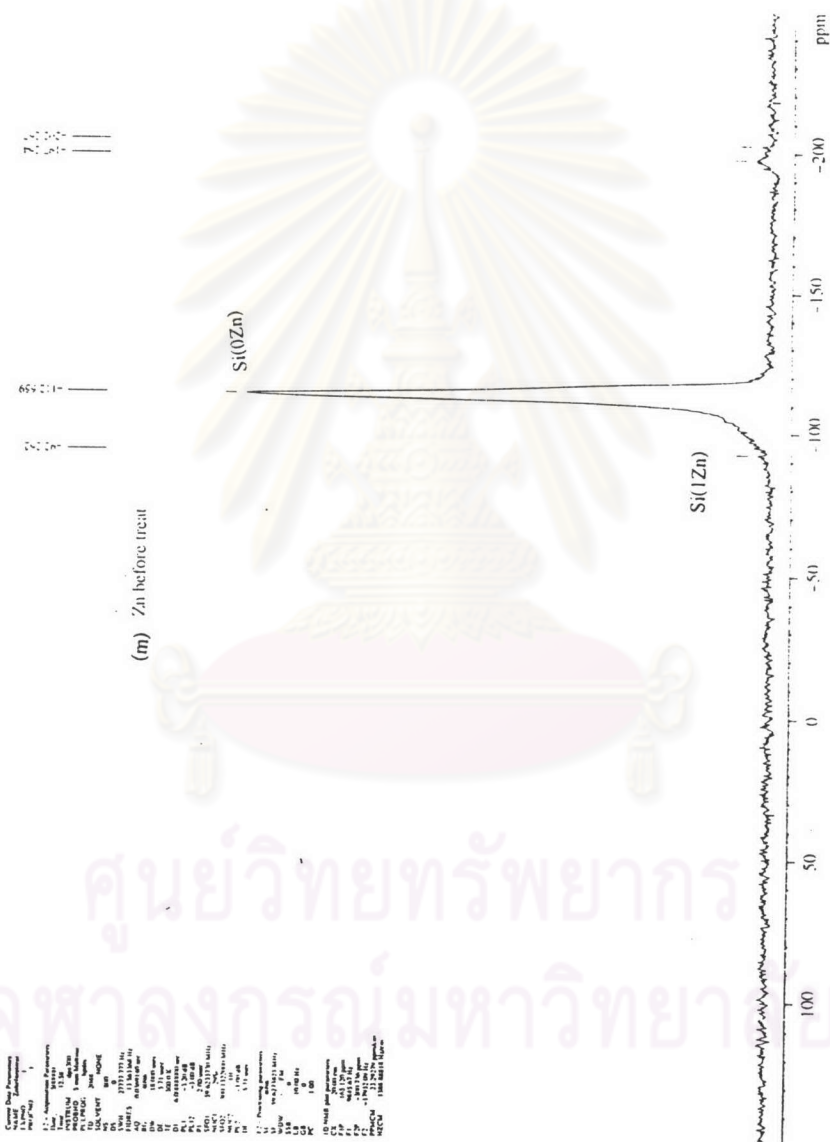
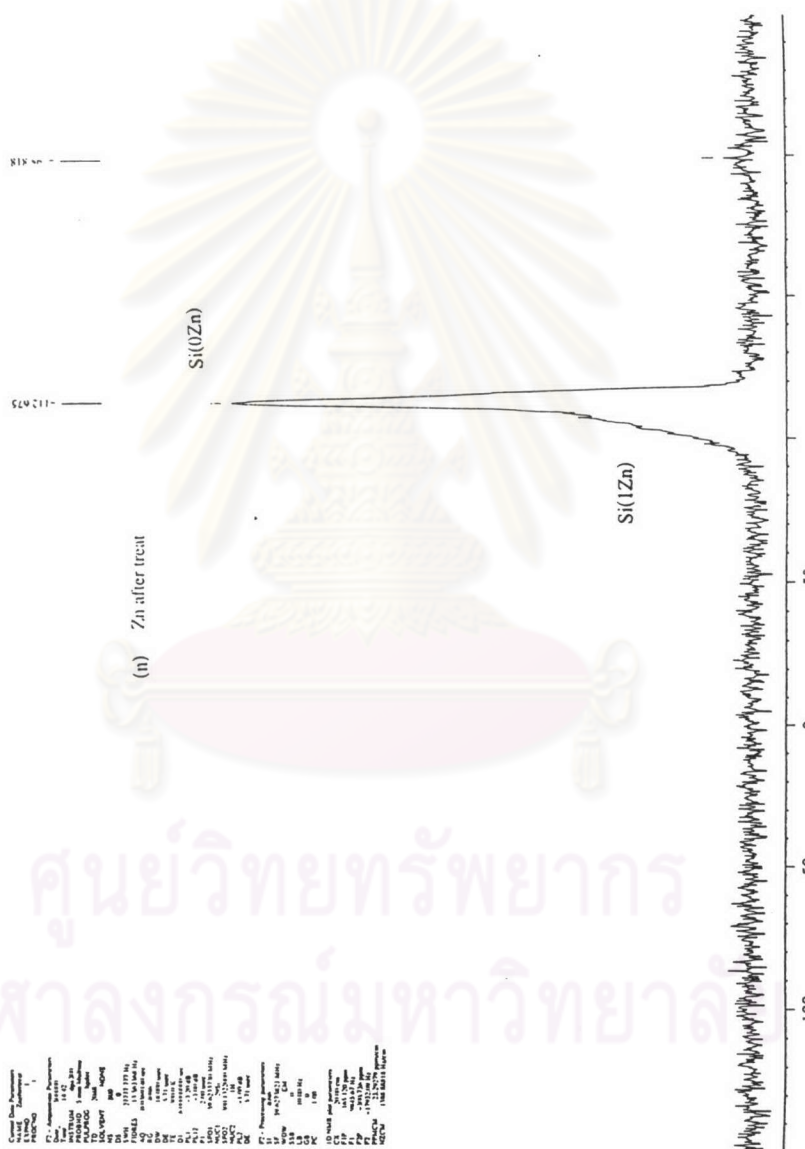


Figure S.3 ²⁹Si NMR Spectra (continued)

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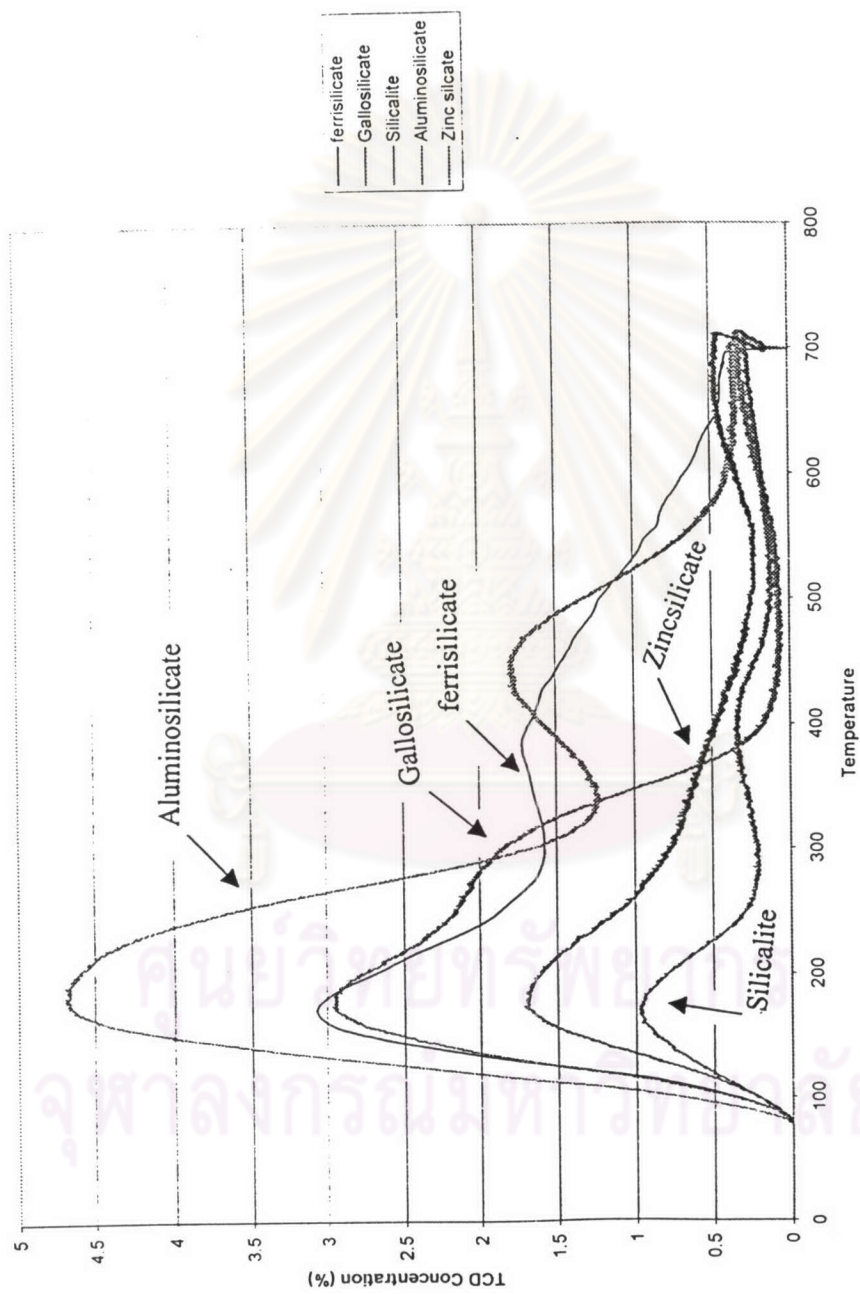


Figure 5.4 TPD (NH₃) curve of metallosilicate catalysts

Fe₂O₃ impregnation on silicalite

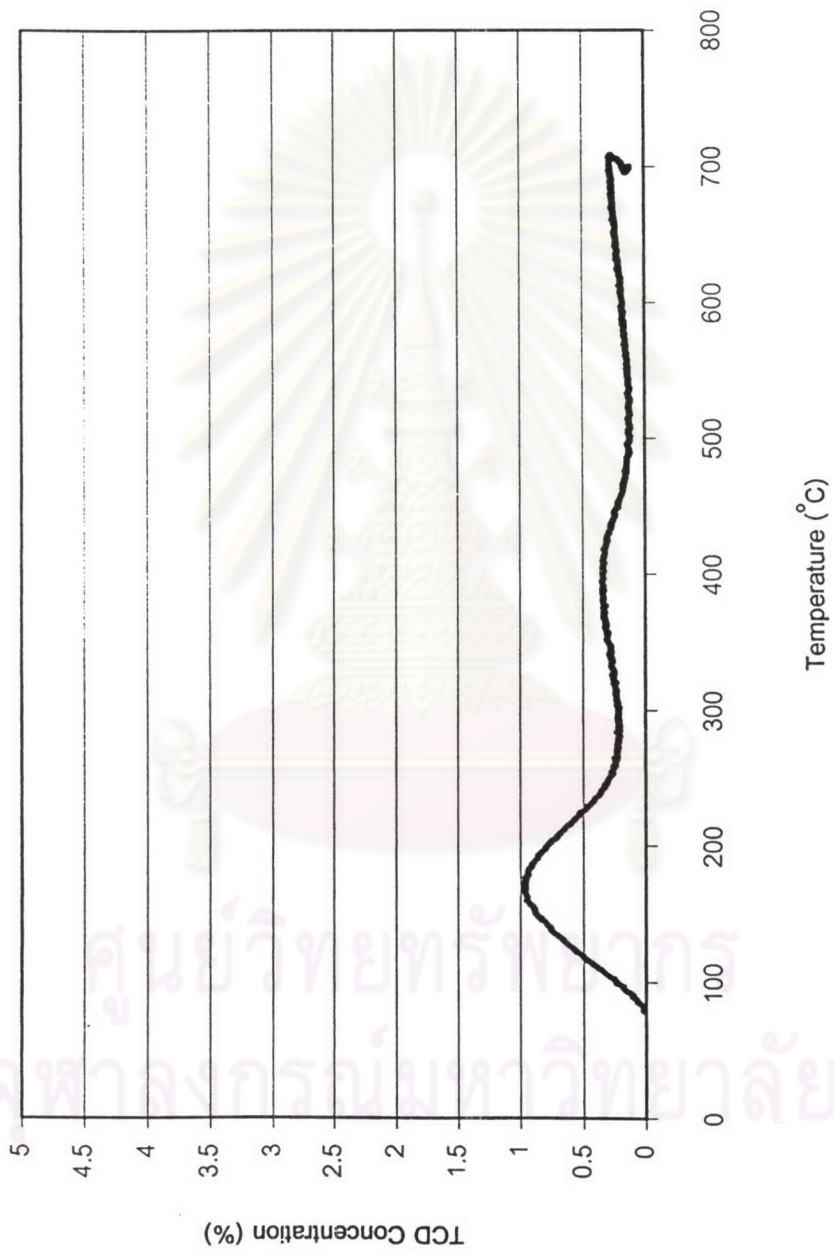


Figure 5.4 TPD (NH₃) curve of metallosilicate catalysts (continued)

5.3 Effect of hydrothermal treatment of the catalysts on crystallinity

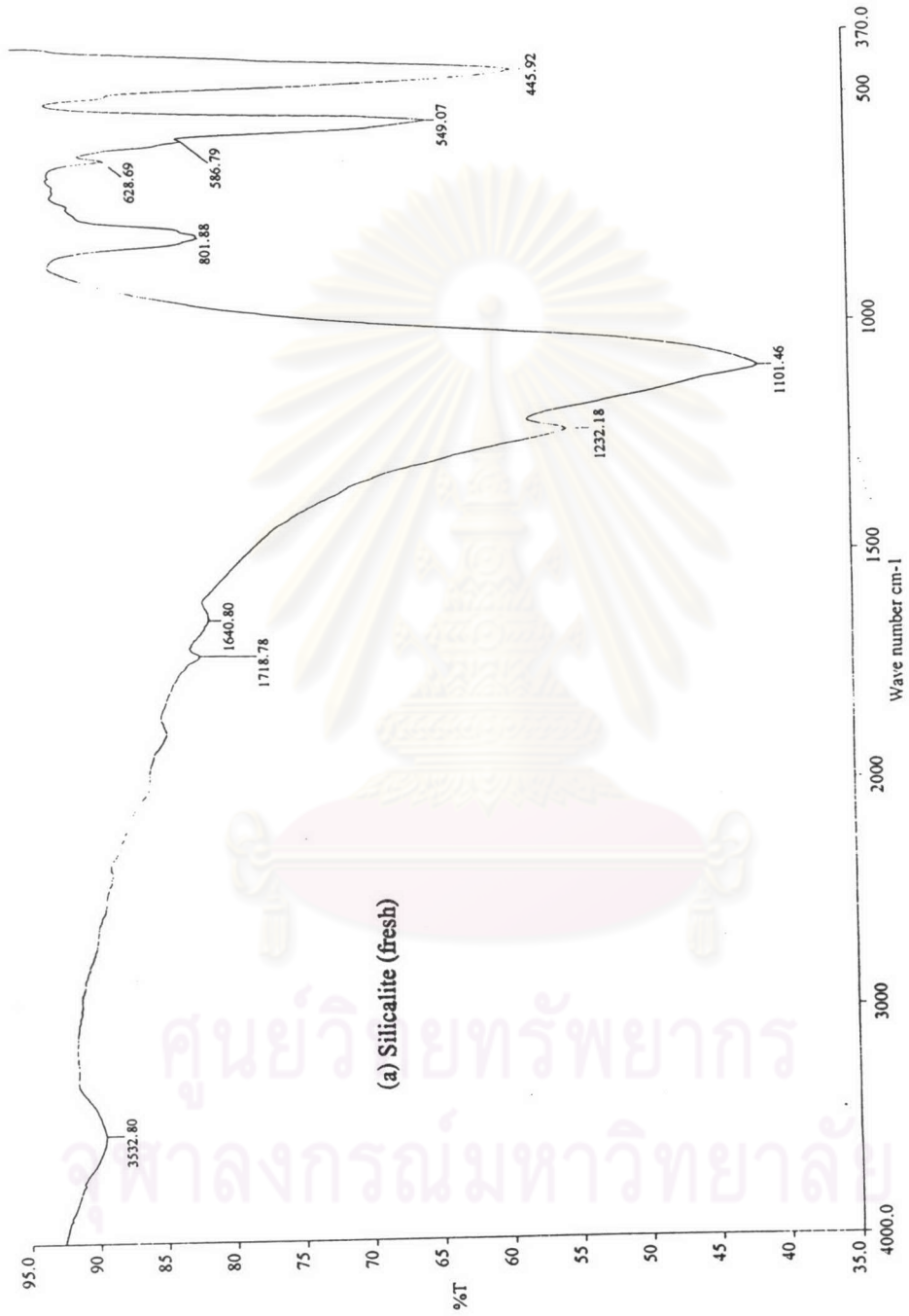
Crystallinity of metallosilicate catalysts are shown in Table 5.1 Crystallinity determined base on XRD profiles, was calculated using the area of the dominant peak, which was compared with that of silicalite (fresh) as a reference. The intensity ratio is generally believed to reflect the crystallinity, i.e., the amount of crystalline zeolite phase in the studied material [82]. The crystallization during the synthesis procedure can increase the intensity of selected XRD pattern peaks since the chemical composition of site occupancy in the crystalline phase will not change during the synthesis process [82]. According to the XRD profiles of the fresh catalysts, in the Table 5.1, in the case of silicalite, it is naturally allowed peak intensities of highest crystallinity because of framework atoms occupying in the same lattice sites [82]. Upon hydrothermal treatment, the silicalite (pretreated) catalyst exhibit a high resistance towards, hydrothermal treatment condition, the crystallinity of the silicalite catalyst is not affected by hydrothermal treatment with slightly decreased (from 100 to 95%) indicating hydrothermal stability of silicalite catalyst better than other metallosilicate catalysts. For H-Al-Silicate (fresh) has high crystallinity since the scattering factors of silicon and aluminum are not very different and, due to the low lattice cation content, the contribution of scattering matter in extra-framework lattice position to the structure factors is generally small compared to that of the framework [82], and Vetrivel [86], studied the Al in ZSM-5 and conclude that Al favors longer bond length than Si. In contrast, isomorphous incorporation of trivalent framework elements (e.g. Fe, Ga) in amounts corresponding to about 2% of the T-atoms affects the peak intensities and give high substitution degrees the crystallinity of zeolites but less than H-Al-Silicate due to the scattering factor of Silicon and Fe or Ga in framework are very different [82]. So, it have very different of strength of chemical bond during metal – oxygen and depend on type of metal in metallosilicate structure on crystallinity. In the sample H-Zn-Silicate is visible, with intensity too decreasing in comparison with that of Silicalilite (fresh) that the crystallinity of H-Zn-Silicate was considerably to reducing. This is suggested that although Zn^{2+} cations atom can incorporation into zeolite framework sites to form metallosilicate structure but its strength of structure have lower than other metal in the same family (i.e. Al, Fe, Ga) because of it have lower strength of chemical bond during Metal-Oxygen as was seen

from table 5.1 and the atomic weight of Zn is larger than that of Si and Al, and the Zn-O bond is longer than those of Si-O and Al-O [70]. So, the crystallinity of H-Zn-Silicate have lower than other metallosilicate catalysts. For all pretreated catalysts, crystallinity of them were considerably reduced following hydrothermal treatment that means having loss of hydrothermal stability and durability at high-temperature. However, we found that H-Zn-Silicate have lowest hydrothermal stability when compared with silicalite. At temperature 600°C in 10 mol% water, 24 hr. of hydrothermal treatment condition of the metallosilicate catalysts (Table 5.1), indicating that the order of strength of hydrothermal stability is Al>Fe>Ga>Zn-MFI, in suggestion with earlier mention based on strength of chemical bond during Metal-Oxygen. After hydrothermal treatment, the hydrogen form of metallosilicate reacts with water at elevated temperatures, massive hydrolysis of metal occurs resulting in the destruction of the framework because too many bonds are broken. The crystallinity of all catalysts were reduced following hydrothermal treatment. Moreover for H-Fe-Silicate, Crystallinity are rapidly decreased (from 73 to 66%) after hydrothermal treatment because of Fe³⁺ environments in the zeolitic structure have less stable against overheating seem to be sites where charge compensation occurs hydrated octahedral (extra-framework) sites after hydrothermal treatment and the hydrothermal treatment condition at increasing temperatures causes dislodgment of iron from framework sites and its intensity is decreasing by hydrothermal treatment, indicating that imperfect crystallization. The decrease of signal intensity by hydrothermal treatment is due to relaxation and reduction of framework Fe³⁺ site [83]. In the case of Fe-containing zeolites, the location of iron in the zeolite framework (Fe_f) or outside the framework (Fe_{ef}), that is in the channels and micropores, Fe_{ef} (mostly in the form of Fe₂O₃, much lower than that of Fe_f which is considerably more stable [84]. To summarize it appears that the stability of structure and hydrothermal stability on hydrothermal treatment of metallosilicate catalyst are related to type of metals in metallosilicate structure on crystallinity under hydrothermal condition. However, H-Fe-Silicate may be incorporate into the tetrahedral zeolite framework site of molecular sieve structure during synthesis using EXAFS by Alexis T. Bell and et. al [85]. They found that Fe³⁺ ions can incorporation into zeolite framework sites to form metallosilicate structure. For H-Fe-Silicate is in structure effect to add acidity as seen from TPD-NH₃ (Fig 5.4) and some of substitution of Si in framework with the

second metal such as Al, Zn, Fe and Ga will effect to add acidity too. That, Addition of second metal into structure is addition acidity of silicalite. For TPD-NH₃ curve (Fig 5.4) of Fe₂O₃ impregnation on silicalite, we found that Fe₂O₃ on surface catalyst will not effect to add acidity.

5.4 Infrared Spectroscopy (FT-IR) technique to illustrate the species of metallosilicates

Infrared spectroscopy provides supplementary evidence for framework incorporation of metal. The FT-IR spectra for five samples are shown in Fig.5.5. In all zeolites, symmetric and asymmetric stretching vibrations of the – (Si-O-Si (Al))_n- group generally appear between 600 and 1250 cm⁻¹ [74]. For H-Fe-Silicate, the broad absorption bands have not appeared at 960 cm⁻¹ to 1100 cm⁻¹. It is well known that the absorption bands at these regions are due to the-(Si-O-Fe)_n- asymmetric vibration of iron incorporated zeolites with tetrahedrally MFI type topology [14, 75, 78]. H-Ga-Silicate, IR spectra recorded from the Ga containing zeolites show the same bands as these recorded on HZSM-5, as shown in Fig.5.5. It is, therefore, evident that the Ga-containing zeolite was of the MFI type. The absorption bands at 1225 and 1098 cm⁻¹ correspond to TO₄ (T is Ga) asymmetric stretching vibration, while those at 880 to 625, 545 and 454 cm⁻¹ correspond to TO₄ (T is Ga) symmetric stretching, double-ring and bending vibrations, respectively [76]. For H-Zn-Silicate, the broad band around 950 cm⁻¹ can be reasonably attributed to a Zn-O-Si vibration with the incorporation of Zn in the framework. The bands at 705 and 797 cm⁻¹ in H-Zn-Silicate, for instance, due to the symmetry stretching vibrations of Si-O-T (T is Zn). This can be ascribed to the incorporation of Zn in the lattice framework, because the atomic weight of Zn is larger than that of Si and Al, and the Zn-O bond is longer than those of Si-O and Al-O [77]. However, from the comparison IR resonance during fresh with pretreated catalyst, they have similarly both before and after pretreatment. This indicating that the hydrothermal condition do not affect to change the structure of catalysts and still maintain MFI type structure. Moreover, the shape of line signal FT-IR spectroscopy of pretreated all metallosilicate catalyst at 600°C were roughly similar to that of fresh silicalite indicating that MFI structure was maintained even after pretreatment at 600°C



a:\silicalite\002 - Silicalite (before treat; MT65746)

Figure 5.5 FTIR Spectroscopy

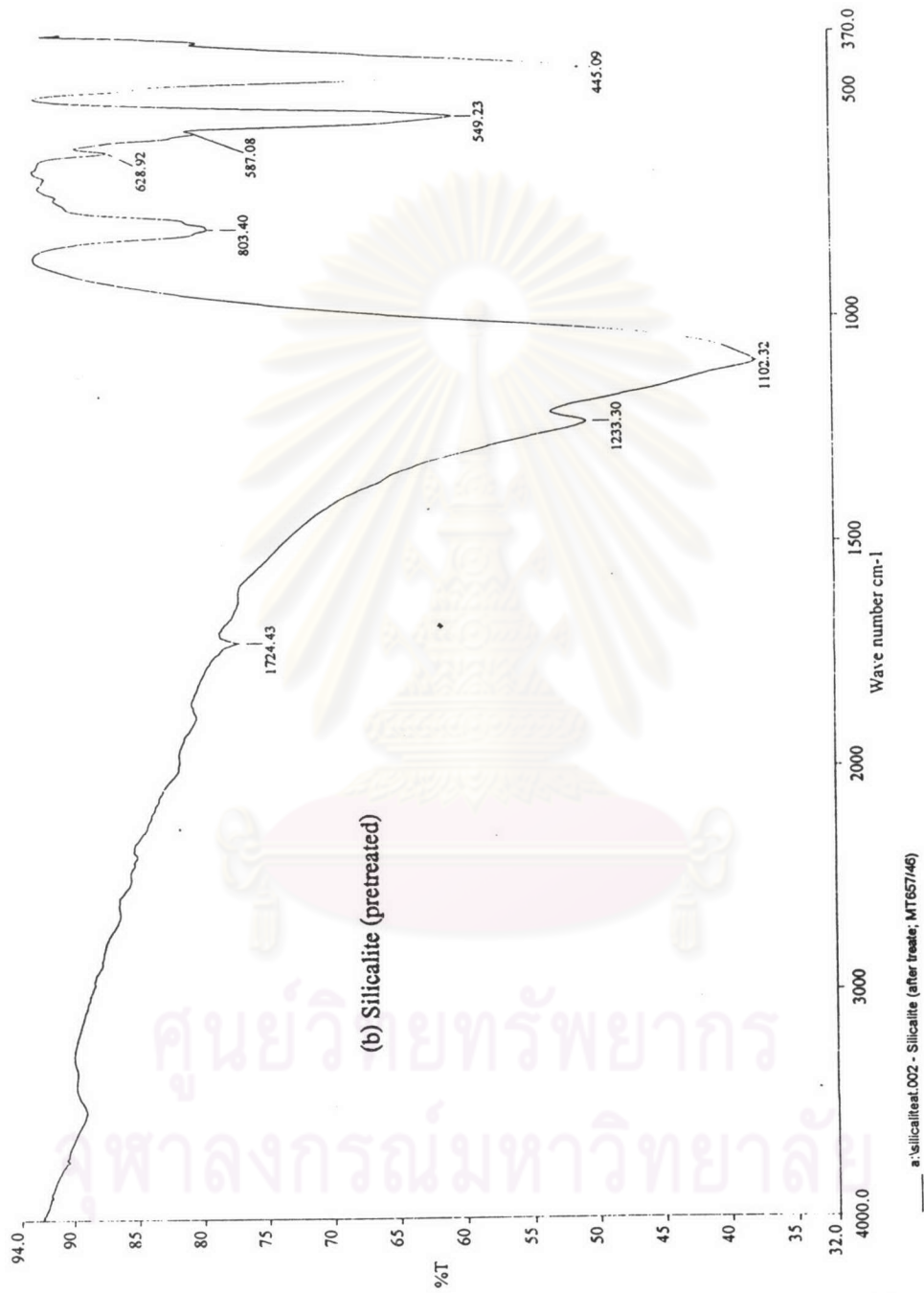


Figure 5.5 FTIR Spectroscopy (continued)

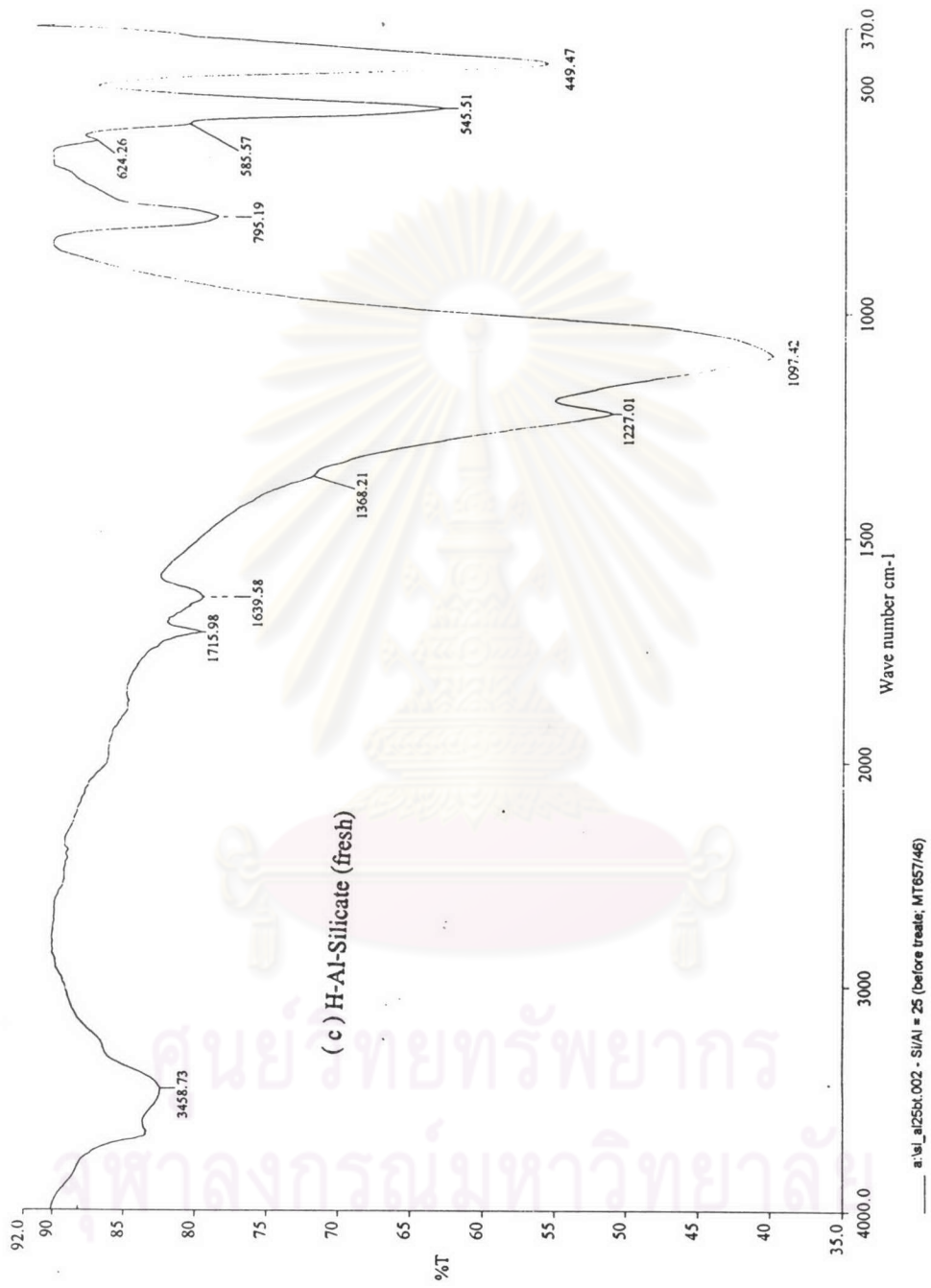


Figure 5.5 FTIR Spectroscopy (continued)

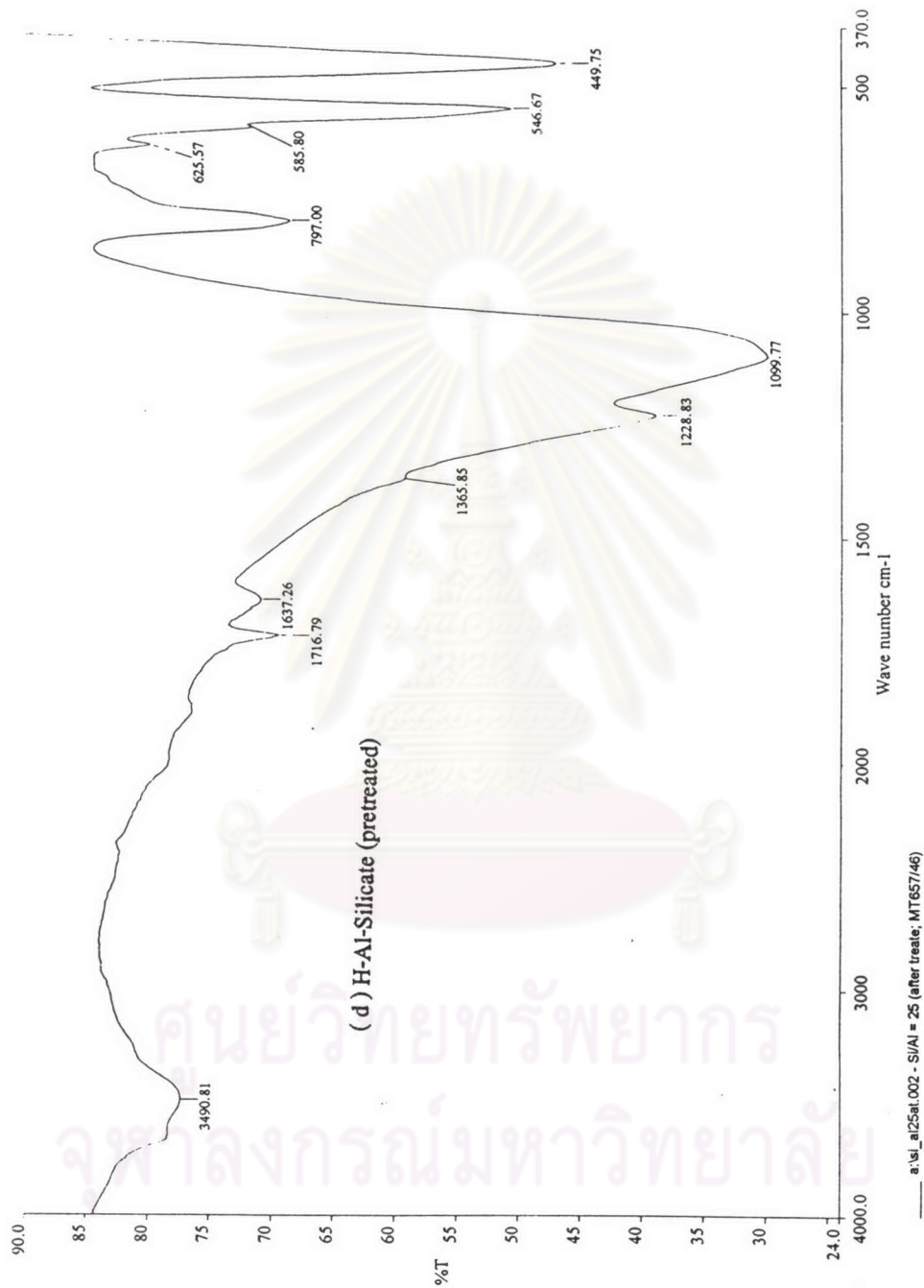


Figure 5.5 FTIR Spectroscopy (continued)

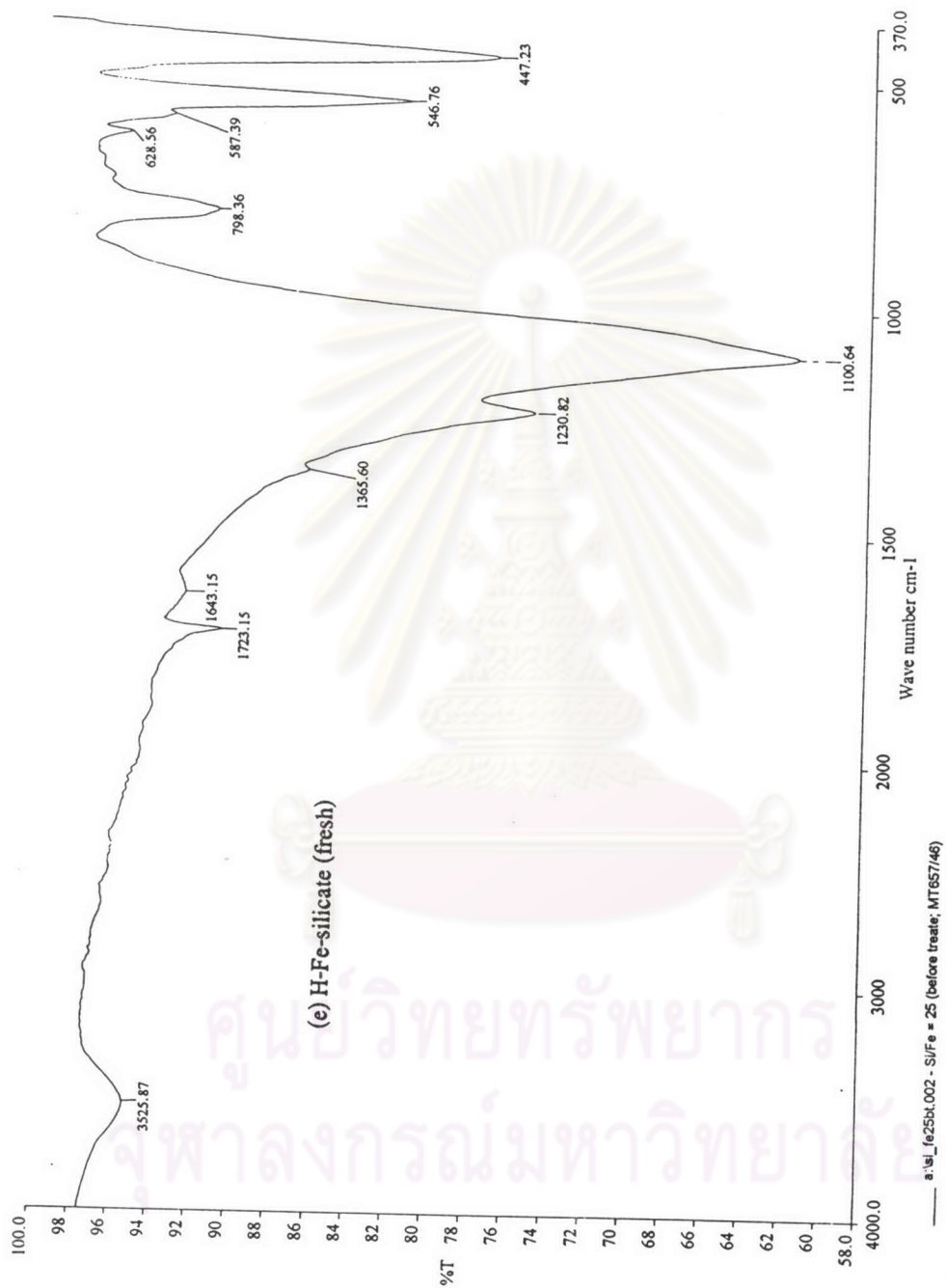


Figure 5.5 FTIR Spectroscopy (continued)

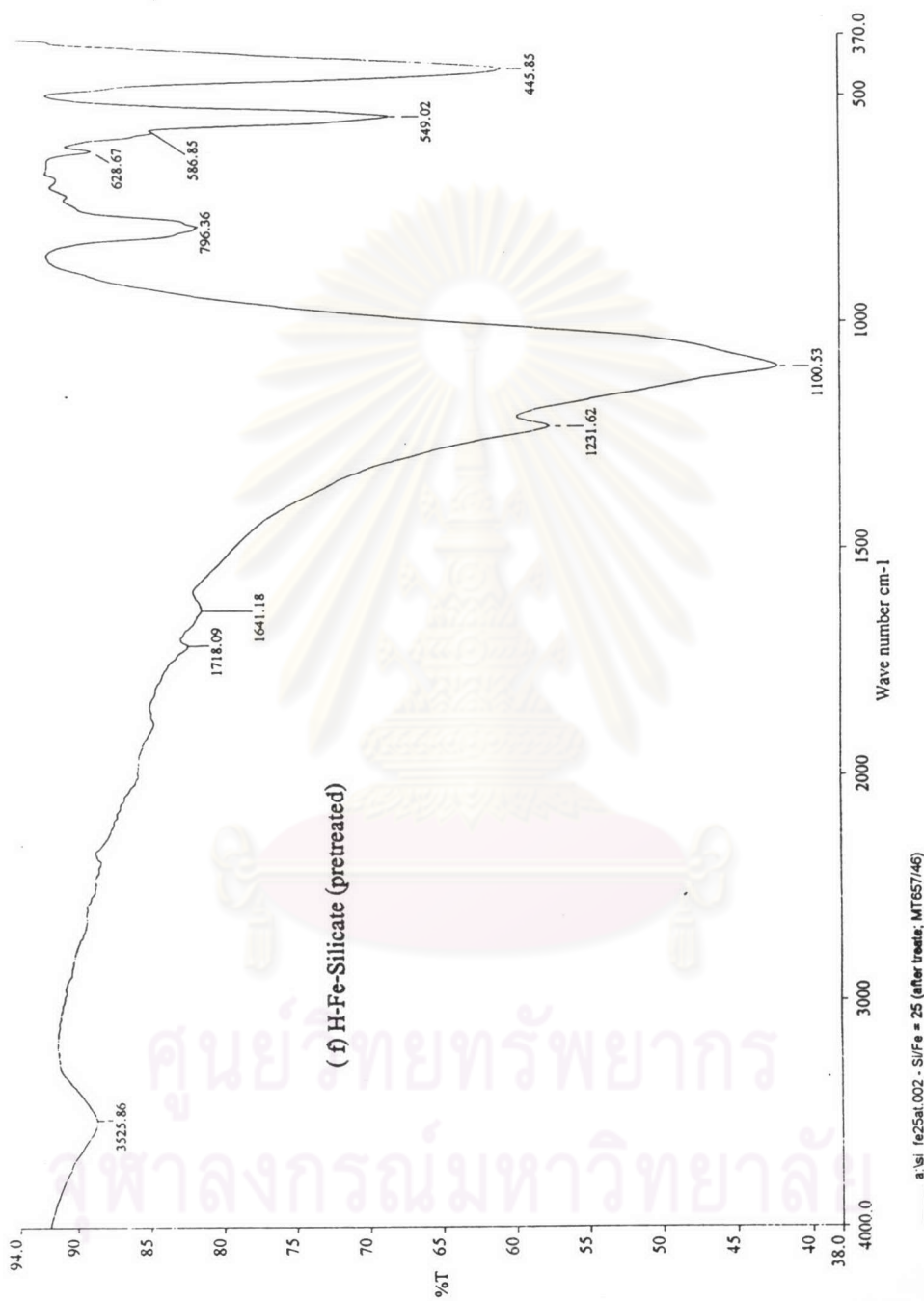


Figure 5.5 FTIR Spectroscopy (continued)

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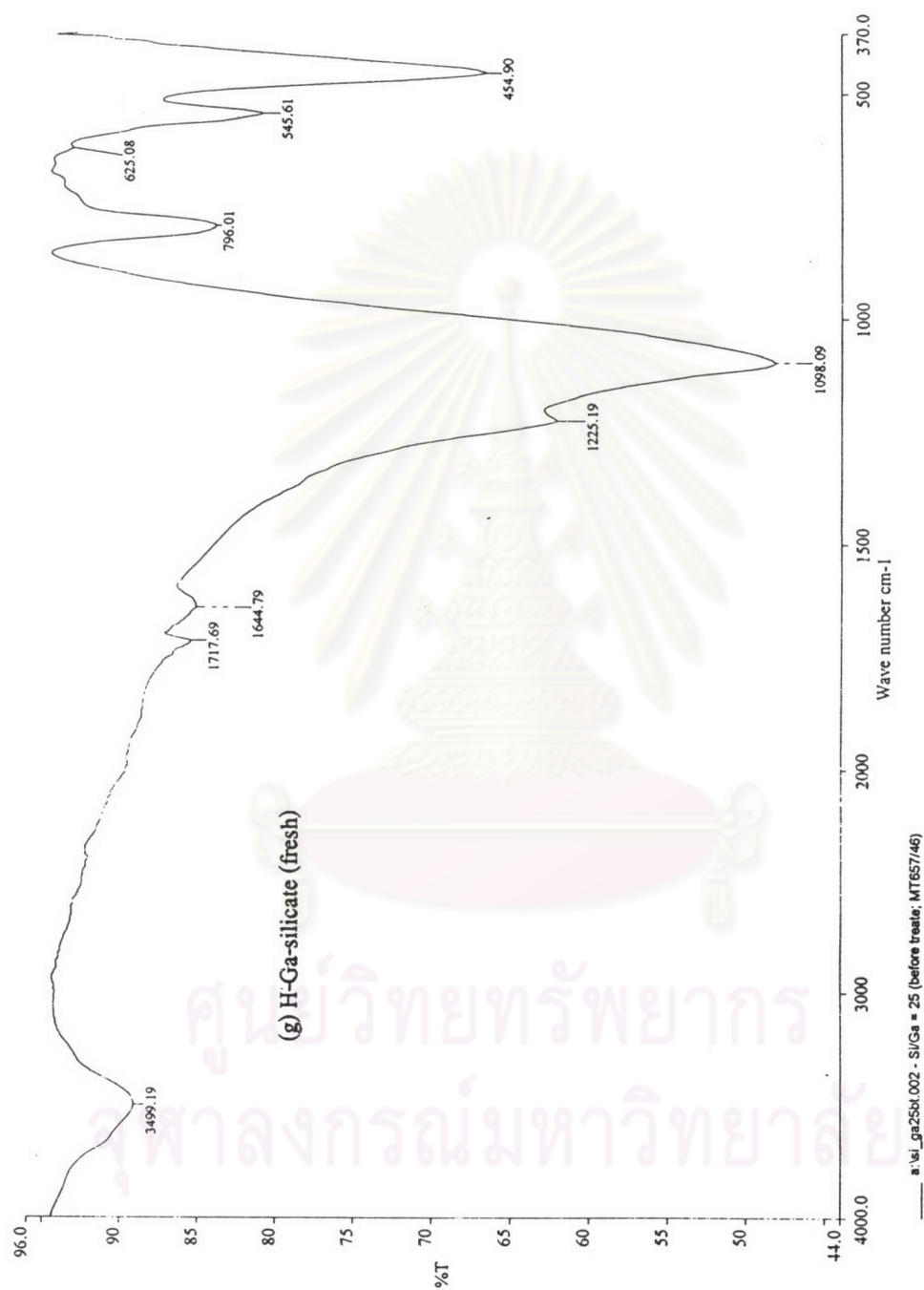


Figure 5.5 FTIR Spectroscopy (continued)

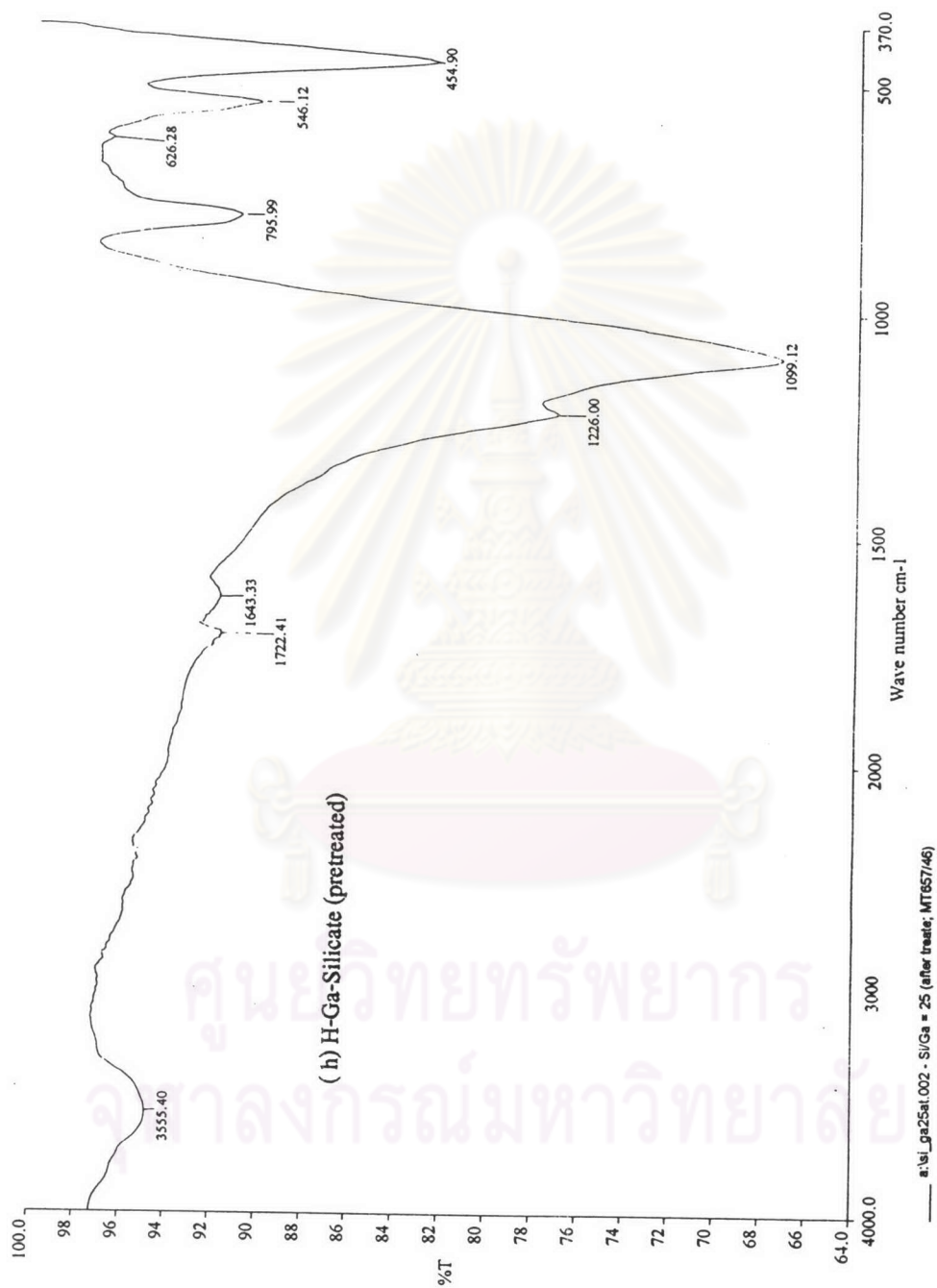


Figure 5.5 FTIR Spectroscopy (continued)

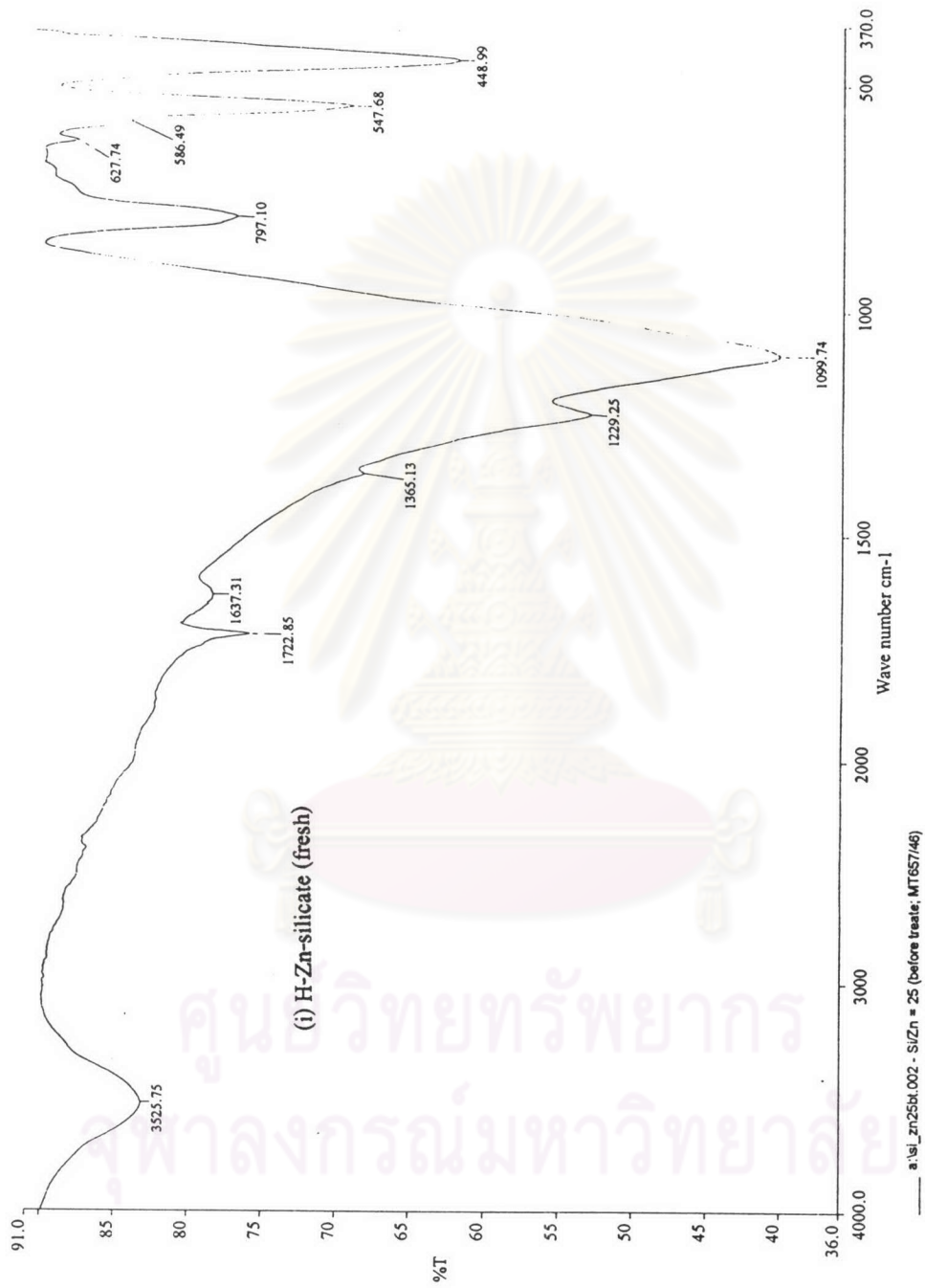
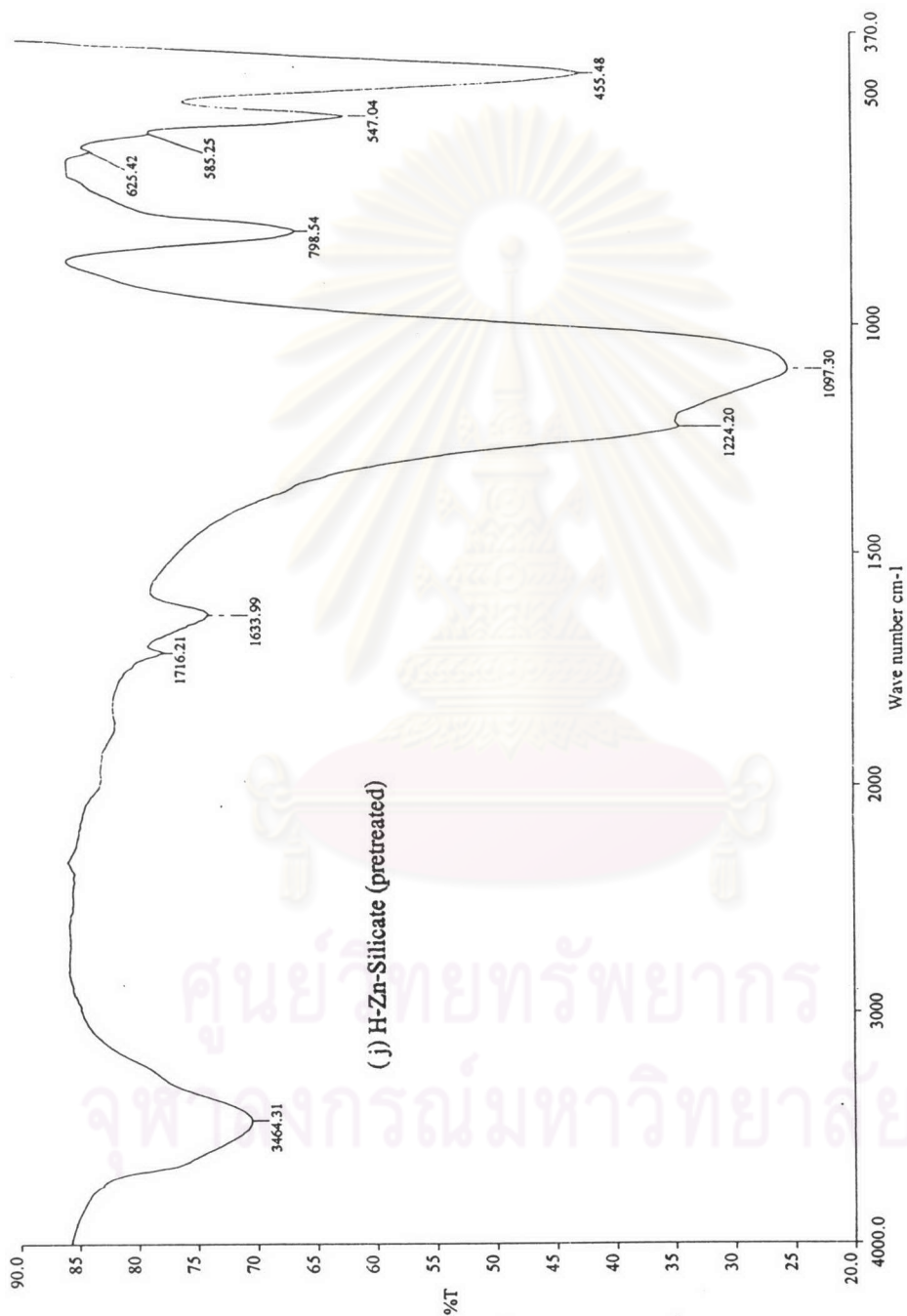


Figure 5.5 FTIR Spectroscopy (continued)



a:\sl_zn\25sat.002 - Si/Zn = 25 (after treat); MT657/46

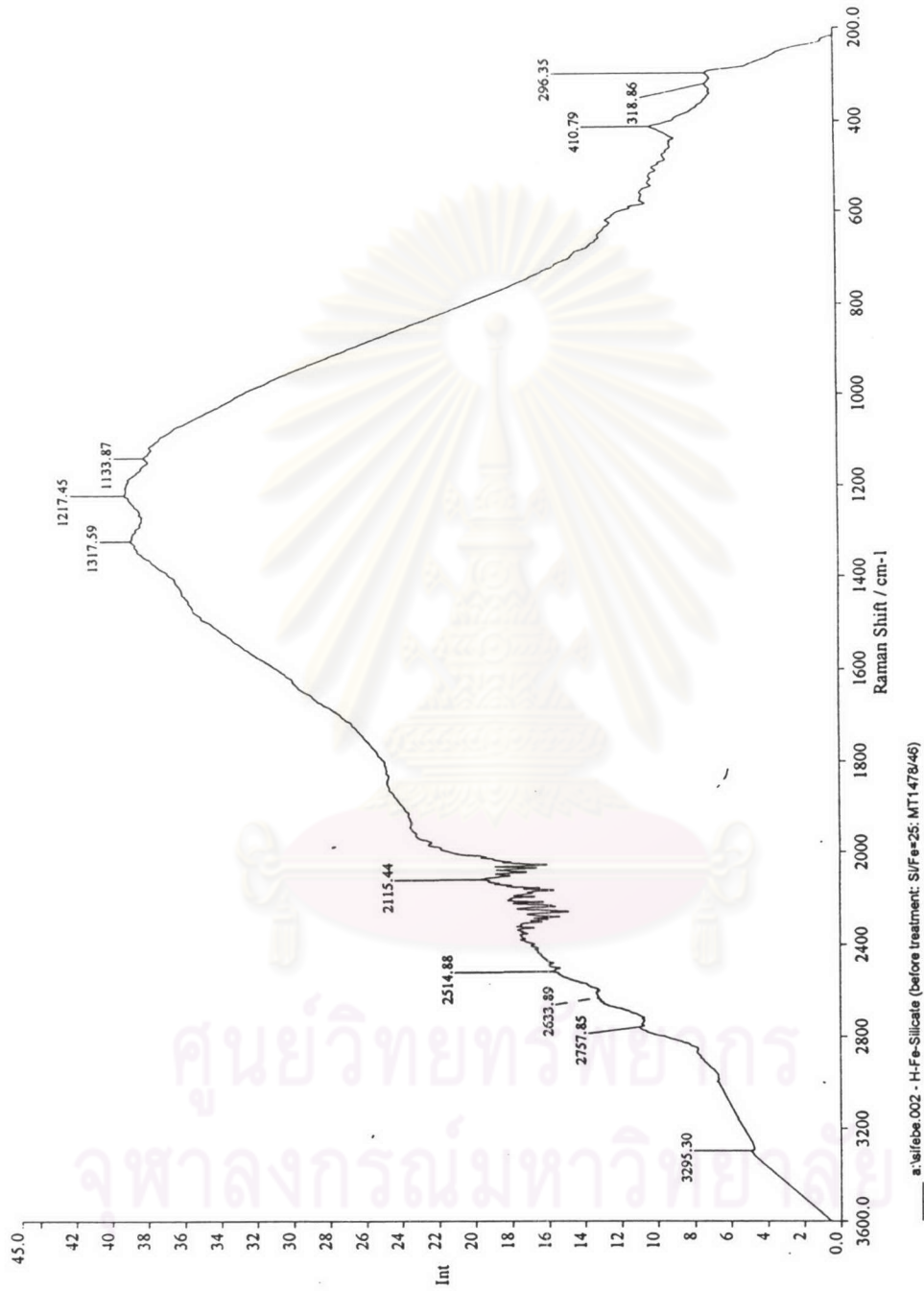
Figure 5.5 FTIR Spectroscopy (continued)

5.5 FT-Raman Spectroscopy technique

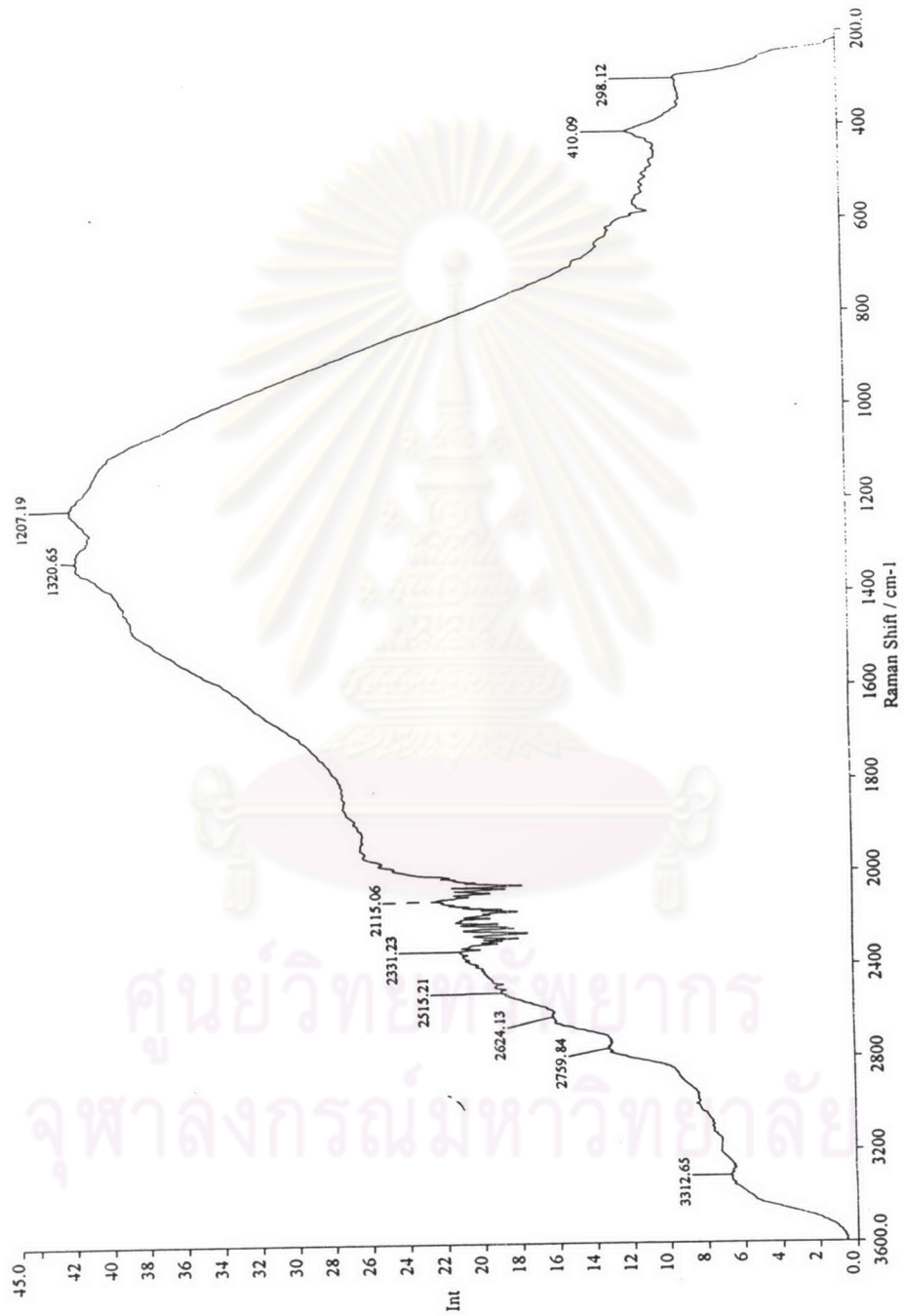
This research was explained completely by FT-Raman Spectroscopy. From ^{29}Si MAS NMR spectra of H-Fe-Silicate, Fe^{3+} can not incorporate into the tetrahedral zeolite framework site but it is in the form of hematite (Fe_2O_3) as seen from FT Raman Spectroscopy of H-Fe-Silicate (Fig 5.6 a, b) when compared with hematite reference (Fig 5.7) [80] that they have similar and peak appear at resonance 296.35 cm^{-1} , 410.79 cm^{-1} and 1317.59 cm^{-1} . For FT-Raman of H-Zn-Silicate (Fig 5.6 c, d) is not similar with peak resonance of ZnO (Fig 5.8 b) [81] which appear at resonance 335 cm^{-1} and 441 cm^{-1} . This indicates that H-Zn-Silicate have attachment of Si-O-Zn which have not ZnO. Ft-Raman of H-Ga-Silicate (Fig 5.6 e, f) is not similar with peak reference of Ga_2O_3 (Fig 5.9) which appear at resonance 1056.61 cm^{-1} . This indicates that H-Ga-Silicate have attachment of Si-O-Ga into framework which does not Ga_2O_3



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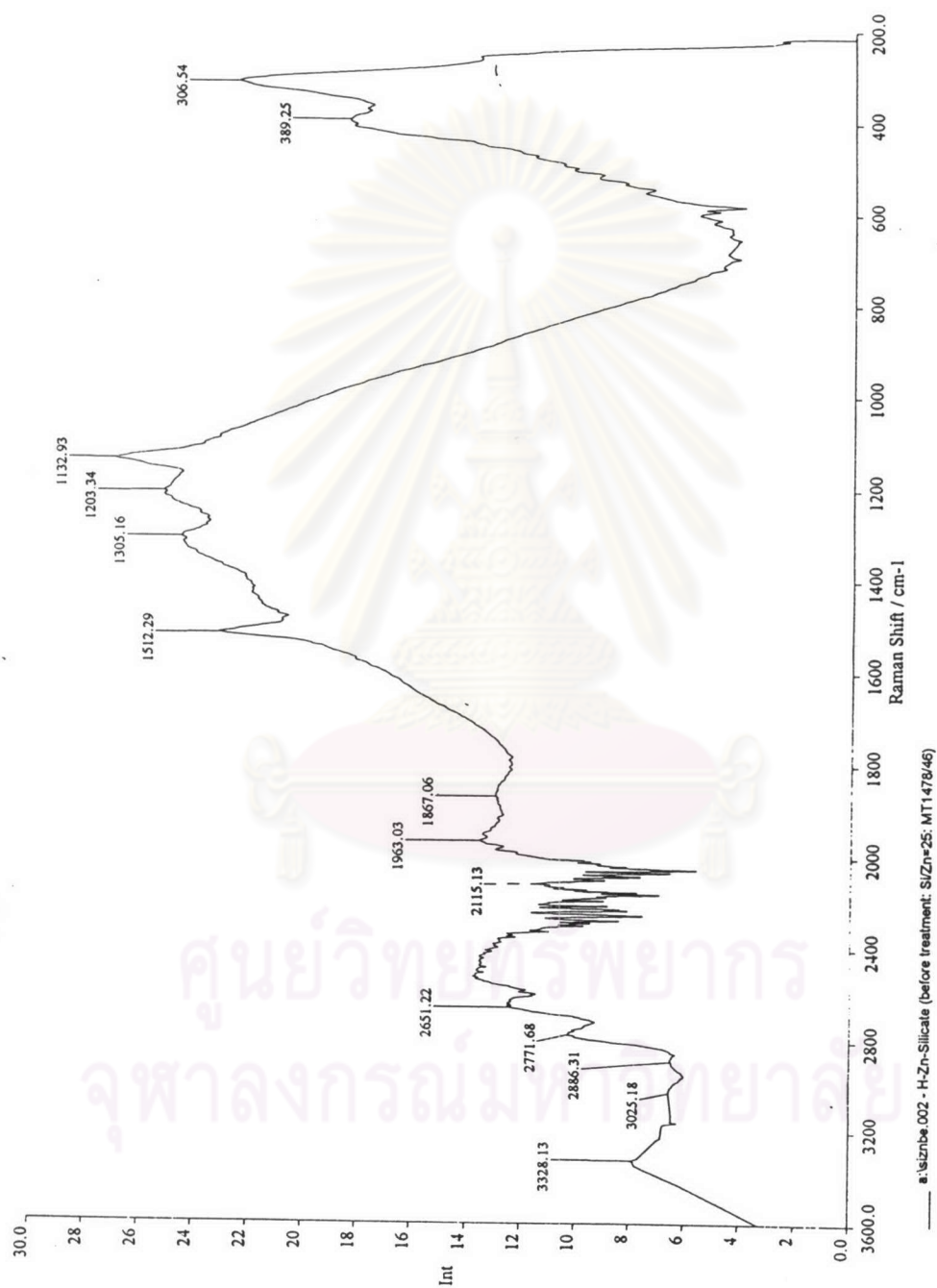


a) Figure 5.6 FT-Raman Spectroscopy of H-Fe-Silicate (fresh)



a:\sifaaf\002 - H-Fe-Silicate (after treatment: SiFe=25: MT1479\46)

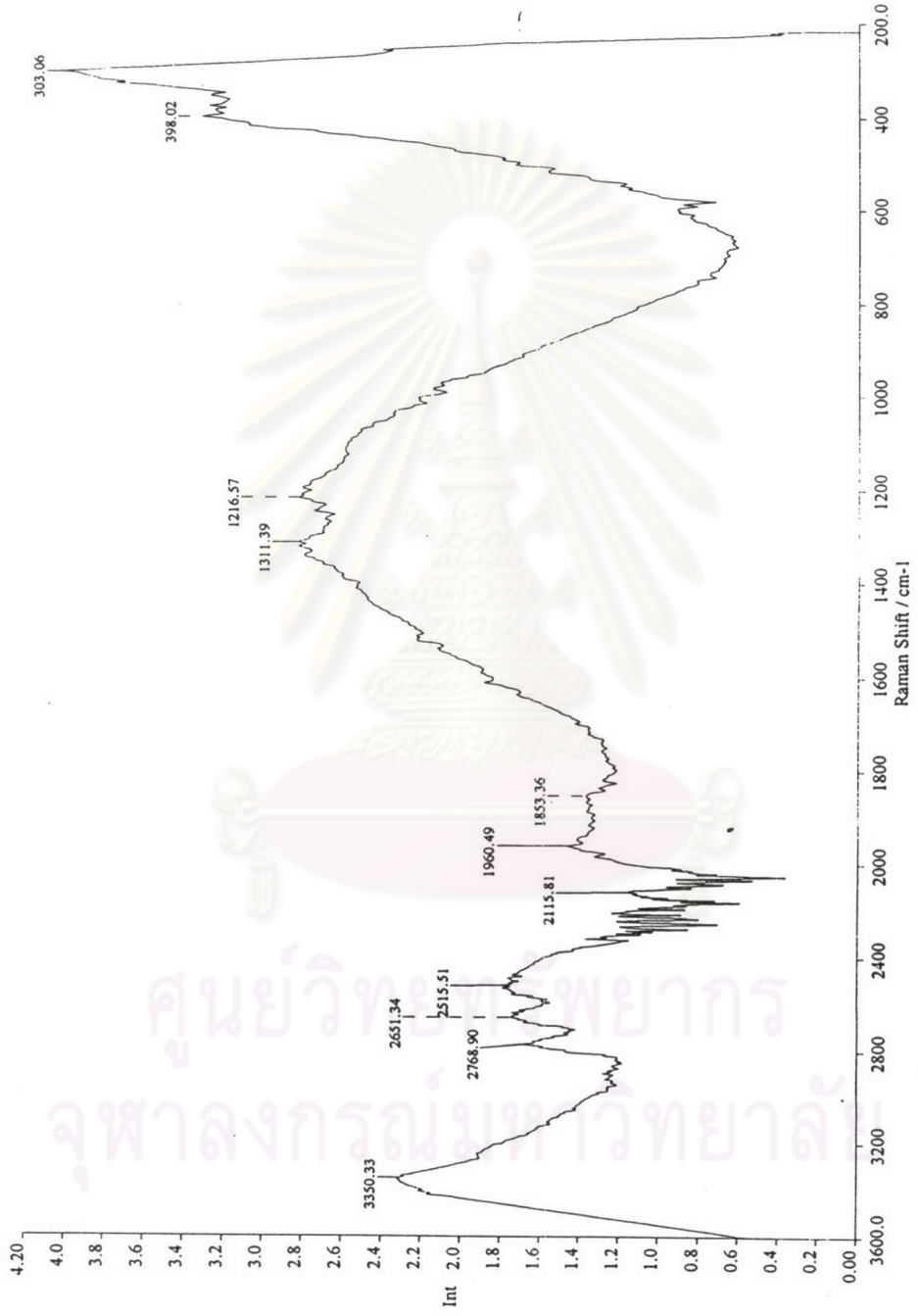
b) Figure 5.6 FT-Raman Spectroscopy of H-Fe-Silicate (pretreated)



c) Figure 5.6 FT-Raman Spectroscopy of H-Zn-Silicate (fresh)

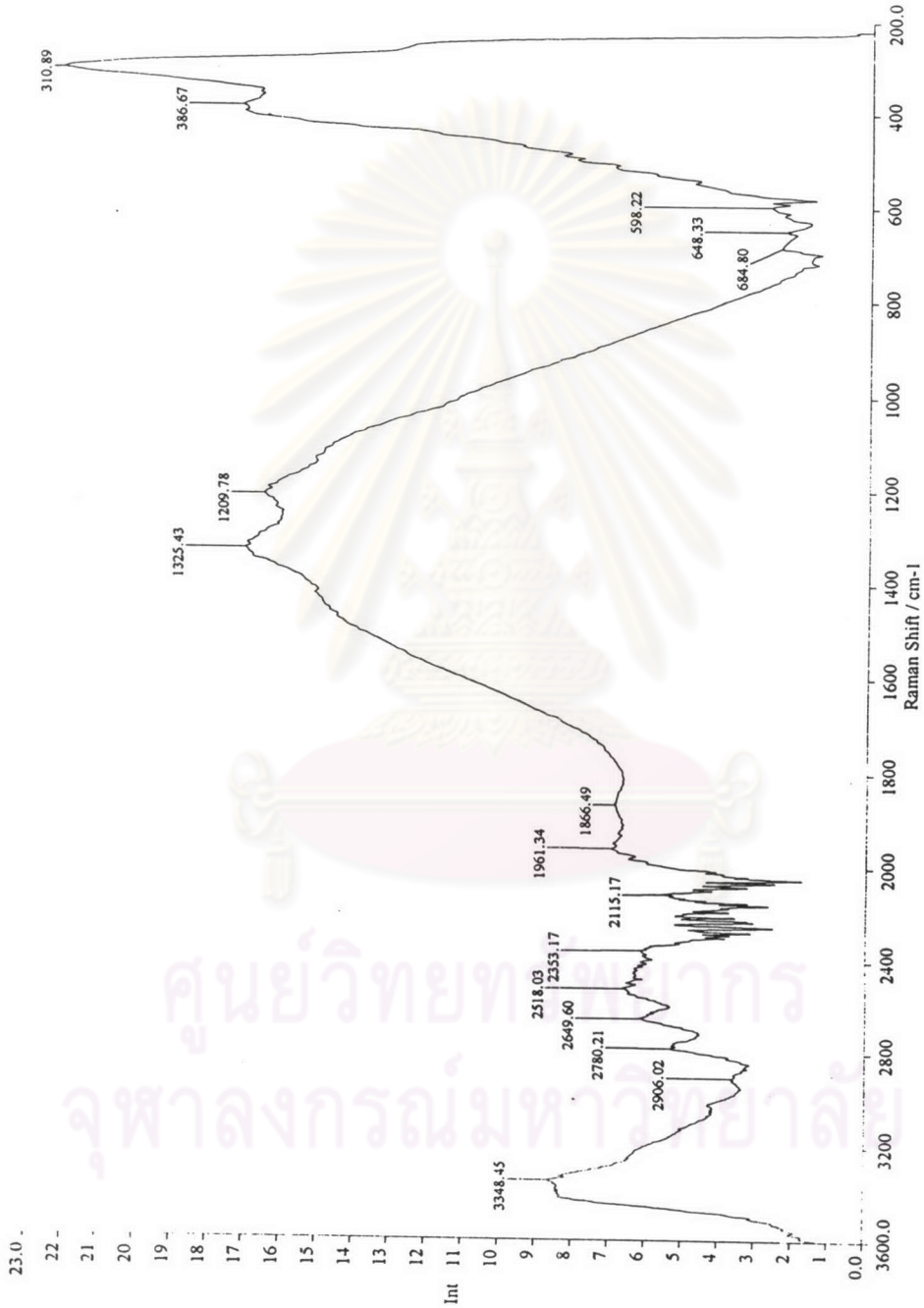
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— a:\sizebe 002 - H-Zn-Silicate (before treatment: Si/Zn=25: MT11478/46)



— a:\signal\002 - H-Zn-Silicate (after treatment: Si/Zn=25; MTT1478/46)

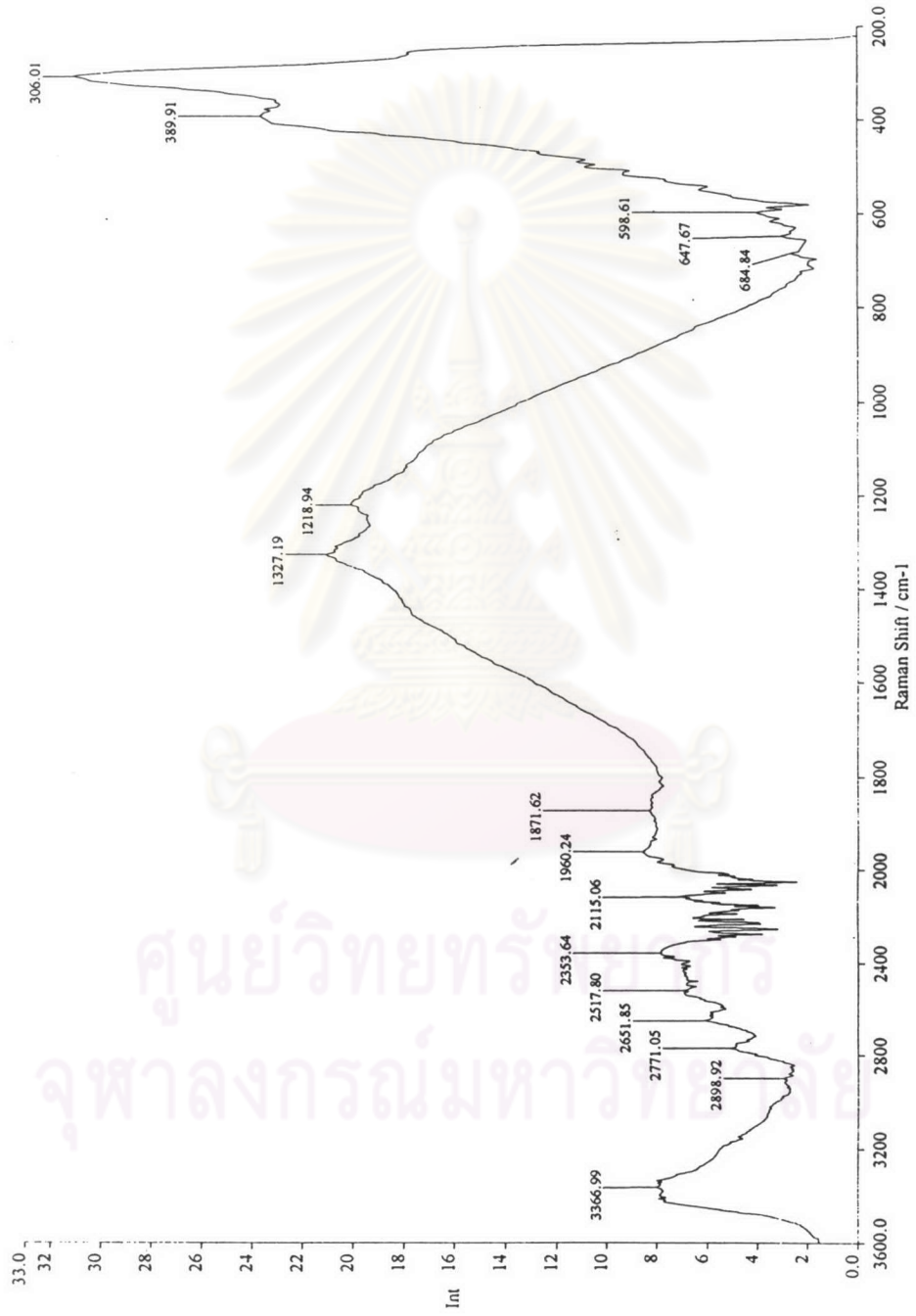
d) Figure 5.6 FT-Raman Spectroscopy of H-Zn-Silicate (pretreated)



a:\sigabe.002 - H-Ga-Silicate (before treatment; Si/Ga=25; MT1478/46)

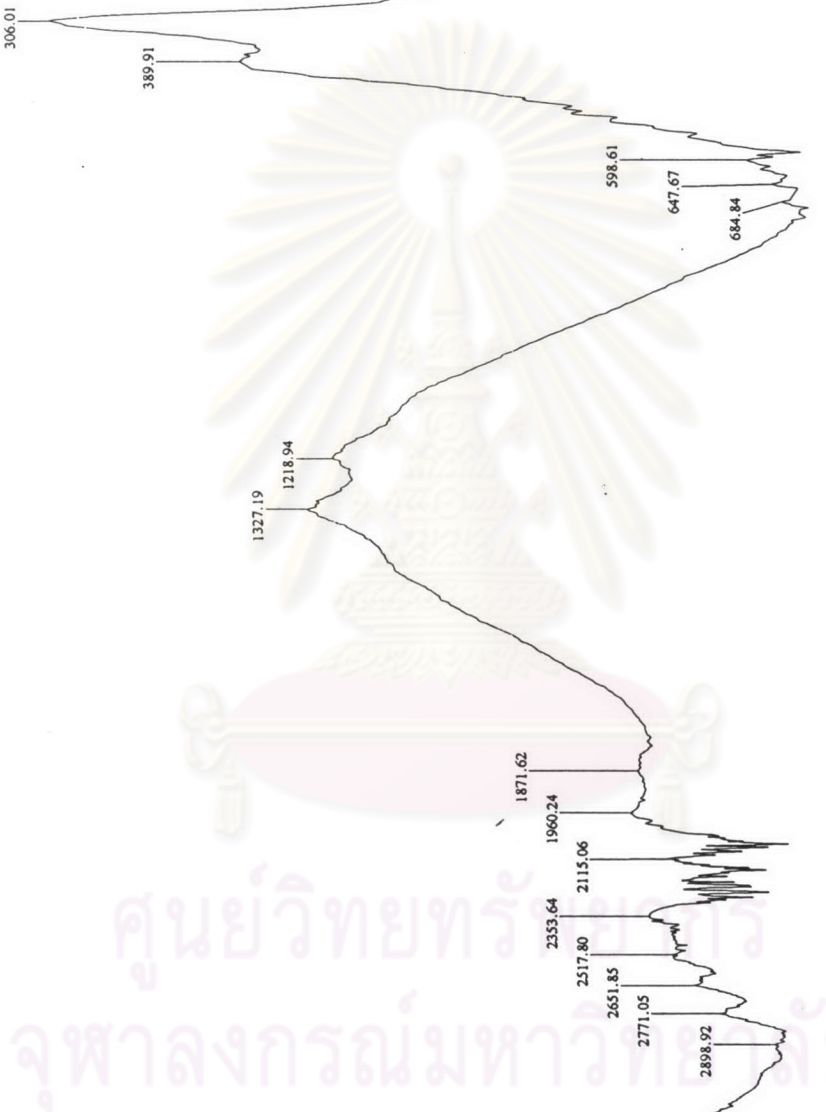
e) Figure 5.6 FT-Raman Spectroscopy of H-Ga-Silicate (fresh)

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a:\sigasf.002 - H-Ga-Silicate (After treatment, Si/Ga=25; MT1478/46)

f) Figure 5.6 FT-Raman Spectroscopy of H-Ga-Silicate (pretreated)



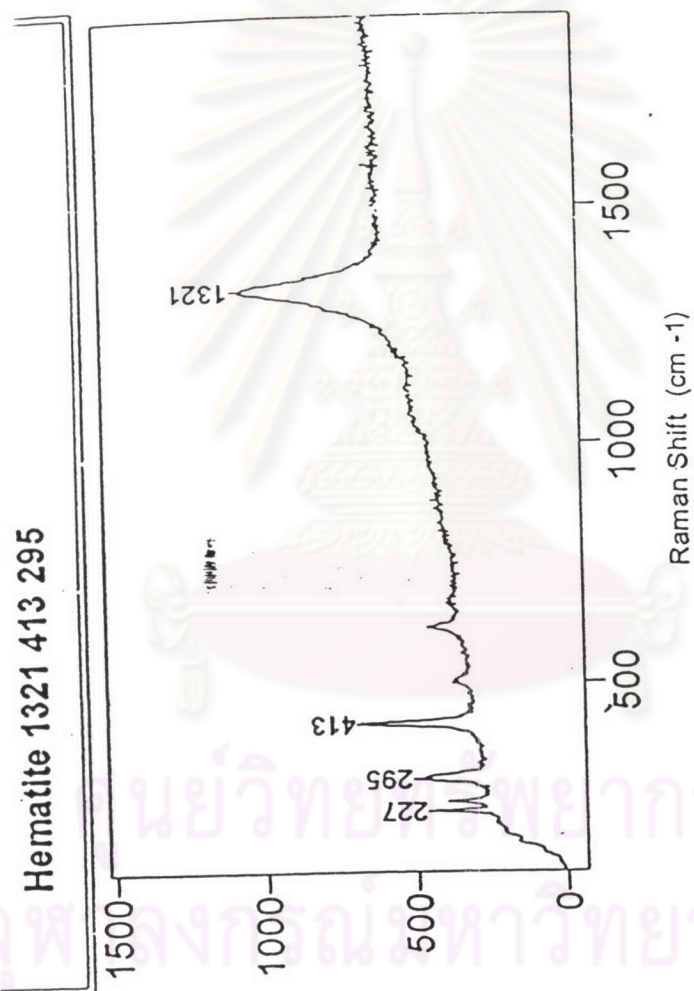
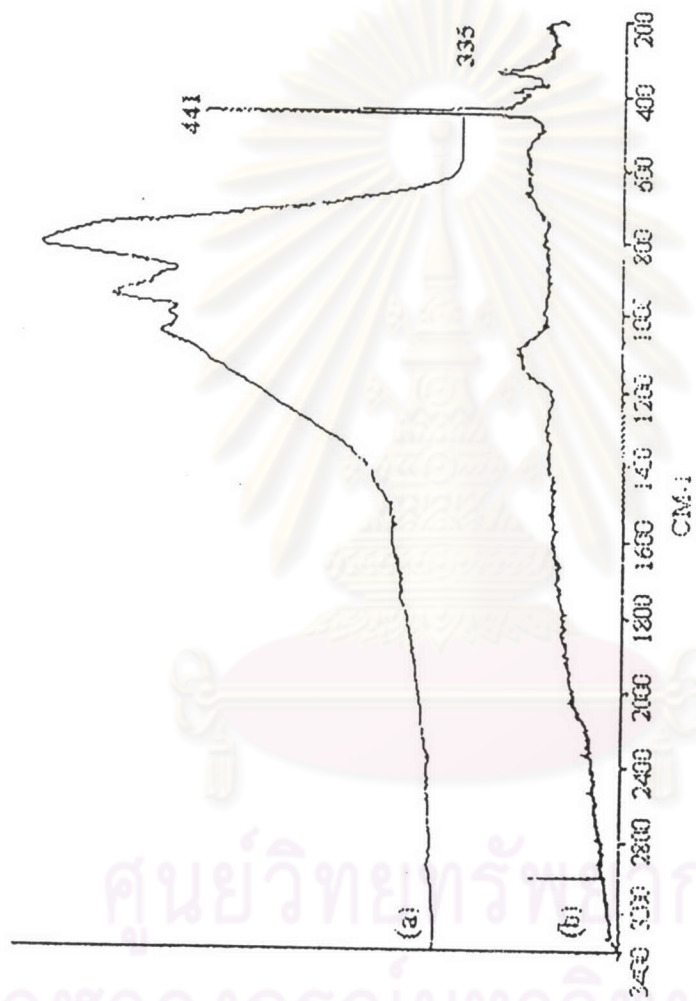
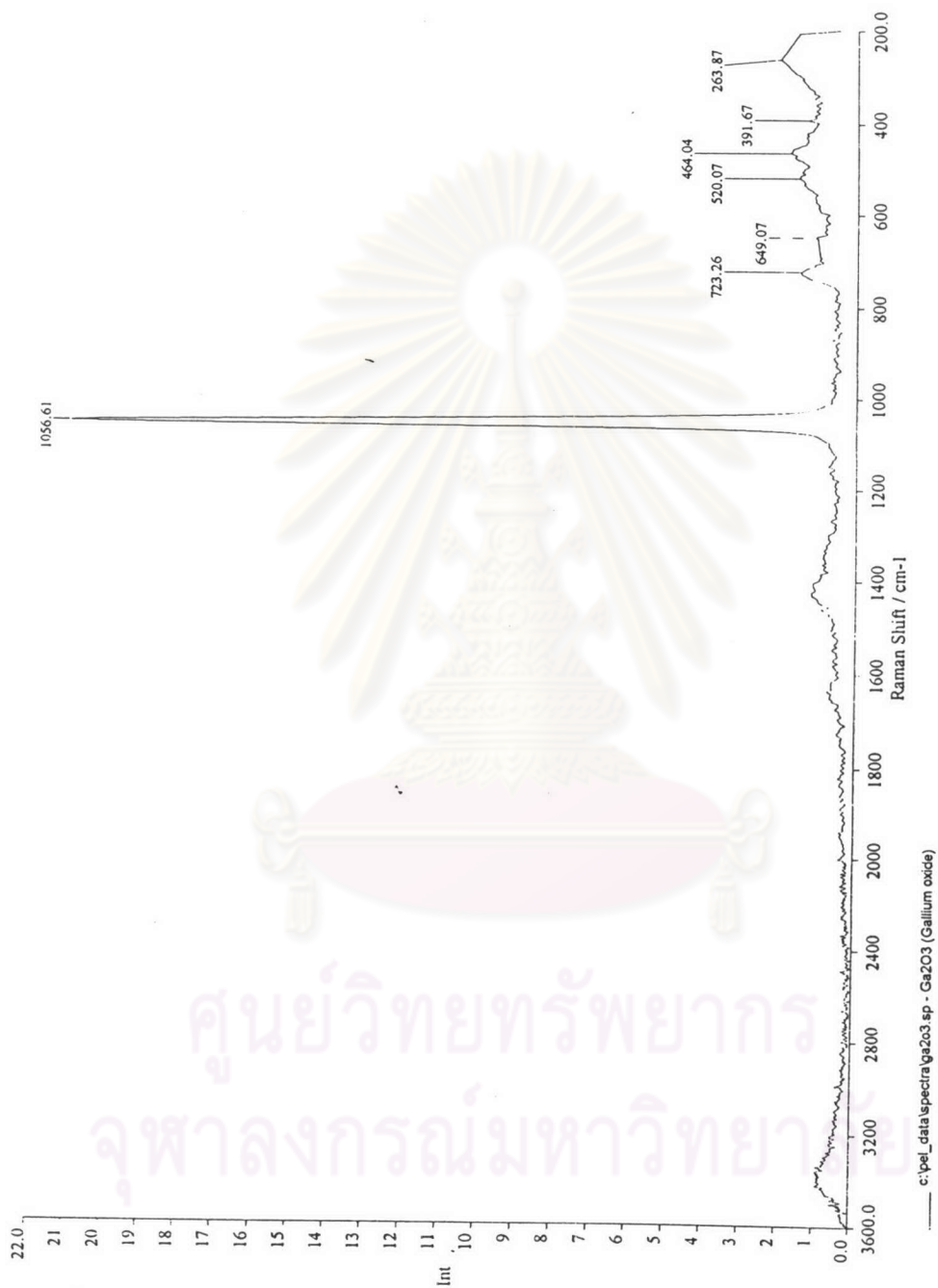


Figure 5.7 Reference of hematite



Absorbance FT-IR (a) and FT-Raman
(b) Spectra of Zinc Oxide

Figure 5.8 Reference of ZnO

Figure 5.9 Reference of Ga₂O₃