

CHAPTER V

RESULTS AND DISCUSSION

This chapter is divided into two sections. The first section, section 5.1, concerns about the characterization results of silica-modified aluminas. The second section, section 5.2, concerns about the discussion from the results.

5.1 RESULTS

The results are divided into two sections. The first section, section 5.1.1, concerns about the properties of silica-modified alumina obtained by one pot synthesis in toluene and 1-butanol at various TEOS contents in starting mixture. The second section, section 5.2.2, concerns about the comparison between silica-modified alumina obtained by one pot synthesis in toluene that had water in the gap between the beaker and the autoclave wall and one pot synthesis in 1-butanol.

5.1.1 Catalyst characterization

(1). Determination of composition content of silica-modified alumina

The results of silica-modified alumina at various silicon contents, which are determinant by Atomic Absorption Spectroscopy, are shown in Table 5.1.

Table 5.1 : Elemental analysis of the products

AIP/TEOS weight ratios	abbreviation	Aluminum (wt%)	Silicon (wt%)	Al/Si atomic ratio
Prepare in toluene				
1	TAS1	21	13.6	1.6
2	TAS2	32	11.8	2.8
8	TAS8	40	4.4	9.4
15	TAS15	47	1.8	27.1
30	TAS30	44	0.9	53.7
Prepare in 1-butanol				
1	BAS1	25	17.7	1.5
2	BAS2	35	14.2	2.6
8	BAS8	42	4.7	9.3
15	BAS15	45	1.9	24.6
30	BAS30	48	1.1	45.25
Prepare in toluene but some water (10,30ml) was added in the gap				
8 (10)	H1AS8	39	4.1	9.9
8 (30)	H3AS8	42	4.4	9.9

(2). Determination of the products crystal structure

X-ray Diffraction is a technique, which can identify the crystal structure. The as-synthesized silica-modified aluminas prepared in toluene and 1-butanol are shown in Figure 5.1a and Figure 5.1b.

The XRD pattern of as-synthesized silica-modified aluminas prepared in toluene are shown Fig 5.1a. TAS ∞ , TAS30 and TAS15 exhibited the XRD pattern for γ -alumina. Four dominant peaks appeared at the 2θ values of 38, 43, 47.5 and 68.

When TEOS in the mixture increased, the peaks of χ -alumina became weak and TAS1, TAS2, TAS8 exhibited the XRD pattern for amorphous.

The XRD patterns of as-synthesized silica-modified aluminas prepared in 1-butanol are shown Figure 5.1b. The XRD pattern of BAS_{∞} exhibited the typical for alkyl derivative on boehmite. Which was similar like pseudoboehmite that had five dominant peaks appeared at the 2θ values of 14, 28, 37.5, 50 and 65 but peak at angles $14^{\circ}(2\theta)$ shifted to the lower angle. That shift showed the basal spacing between boehmite layer that had alkyl moiety bond in the structure. The XRD patterns of BAS_{30} and BAS_{15} suggest that these products were mixtures of χ -alumina and pseudoboehmite. With the increased of TEOS in the starting mixture, The intensity became weak. BAS_8 and BAS_2 exhibited the typical pattern for the mixture of amorphous and pseudoboehmite, while BAS_1 was amorphous.

The silica-modified aluminas prepared in toluene were calcined at 600°C . The XRD patterns are shown in Figure 5.2a. TAS_{∞} , TAS_{30} , TAS_{15} exhibited the XRD pattern typical for χ -alumina. While these five dominant peaks were sharper than as-synthesized products showing the clearly product's phase. However when TEOS in the mixture increased, the peak of χ -alumina became weak and TAS_1 , TAS_2 , TAS_8 still exhibited the XRD pattern typical for amorphous.

The silica-modified aluminas prepared in 1-butanol were calcined at 600°C . The XRD patterns are shown in Figure 5.2b. XRD showed that the structure of alkyl derivative on boehmite of BAS_{∞} was decomposed to be alumina. BAS_{30} , BAS_{15} and BAS_8 exhibited the XRD pattern for χ -alumina and spinel phase getting from the decomposition of pseudoboehmite. The six dominant peaks of spinel alumina appeared at the 2θ values of 31, 33, 38, 43, 47.5 and 68. With the increased of TEOS in the starting mixture, The intensity became weak. Therefore BAS_2 exhibited the XRD pattern for the mixture of γ -alumina-like phase or spinel phase and the sample presumably contained amorphous silica but BAS_1 exhibited the XRD pattern typical for amorphous.

The silica-modified aluminas prepared in toluene were calcined at 1000°C. The XRD patterns are shown in Figure 5.3a. TAS ∞ , TAS30, TAS15 and TAS8 exhibited the XRD pattern typical for spinel alumina. But TAS ∞ showed the presence of the α -transformation. TAS8 was phase transformation from amorphous to spinel alumina and small amount of mullite. However when TEOS in the mixture increased, the mullite phase was observed. The XRD pattern of TAS8, TAS2 and TAS1 showed the presence of mullite phase, while TAS1 and TAS2 exhibited the XRD pattern for the mixture between spinel phase and mullite phase.

The silica-modified aluminas prepared in 1-butanol were calcined at 1000°C. The XRD patterns are shown in Figure 5.3b. BAS ∞ , BAS30, BAS15 and BAS8 exhibited the XRD pattern for γ -alumina. BA1, BAS30, BAS15 and BAS8 had phase transformation from χ -alumina to γ -alumina. But BAS ∞ and BAS30 had little peaks that showed phase transformation from γ -alumina to θ -alumina. However when TEOS in the mixture increased, the mullite phase was observed. The XRD pattern of BAS2 and BAS1 showed the presence of mullite phase but BAS2 exhibited the XRD pattern for the mixture of spinel phase and mullite. BAS1 exhibited the XRD pattern for the mixture of mullite phase and amorphous.

The silica-modified aluminas prepared in toluene were calcined at 1150°C. The XRD patterns are shown in Figure 5.4a. TAS ∞ and TAS30 exhibited the XRD pattern typical for the mixture of χ -alumina and α -alumina. That showed the α phase transformation. TAS15 exhibited the XRD pattern for spinel alumina. When TEOS in the mixture increased, the XRD pattern of TAS8, TAS2 and TAS1 showed the presence of mullite phase. TAS8 exhibited the XRD pattern typical for spinel alumina and a little mullite phase. TAS1 and TAS2 exhibited the XRD pattern typical for the mixture of mullite phase and spinel phase.

The silica-modified aluminas obtained in 1-butanol were calcined at 1150°C. The XRD patterns are shown in Figure 5.4b. BAS ∞ and BAS30 exhibited the XRD

pattern for θ -alumina. BAS15 and BAS8 exhibited the XRD pattern for γ -alumina and small amount of θ -alumina. When TEOS in the mixture increased, the mullite phase was occurred from silicon atom that was not incorporate in the lattice of spinel phase. The XRD pattern of BAS1 and BAS2 showed the presence of mullite phase. BAS1 and BAS2 exhibited the XRD pattern for the mixture of mullite phase and spinel phase.



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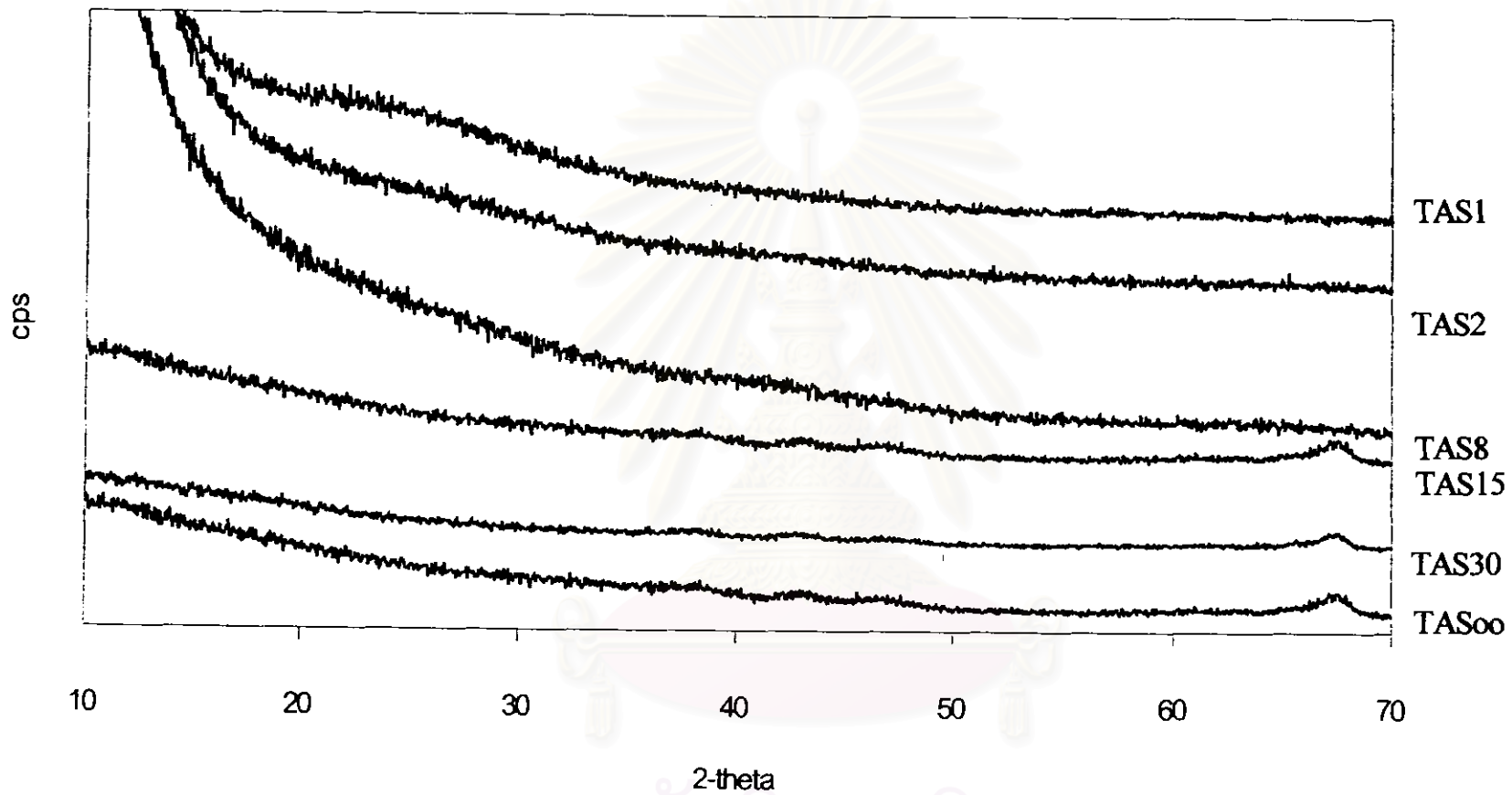


Fig 5.1a: XRD patterns of precursor gels obtained by the reaction of AIP and TEOS in toluene

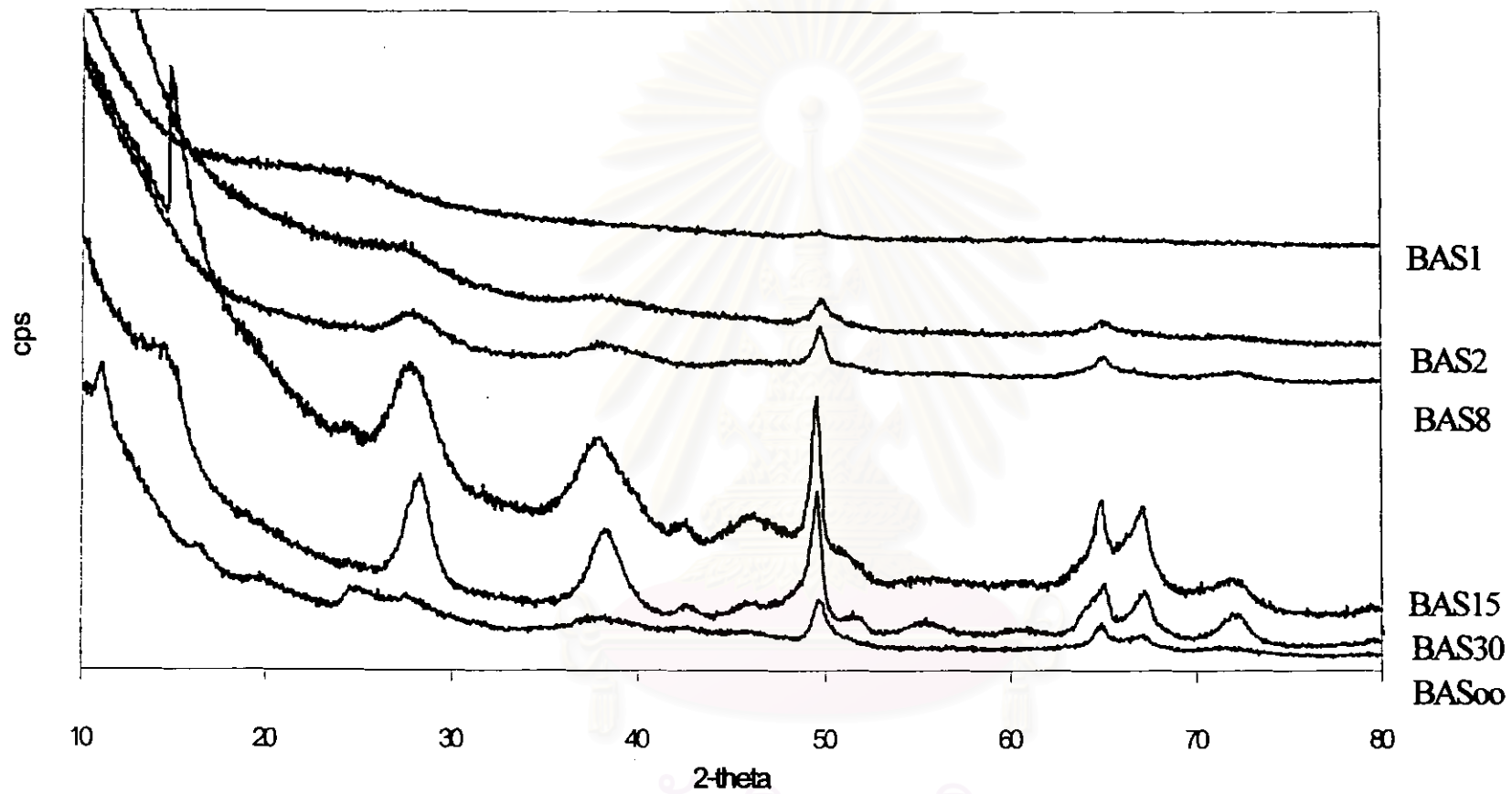


Figure 5.1b: XRD patterns of precursor gels obtained by the reaction of AIP and TEOS in 1-butanol

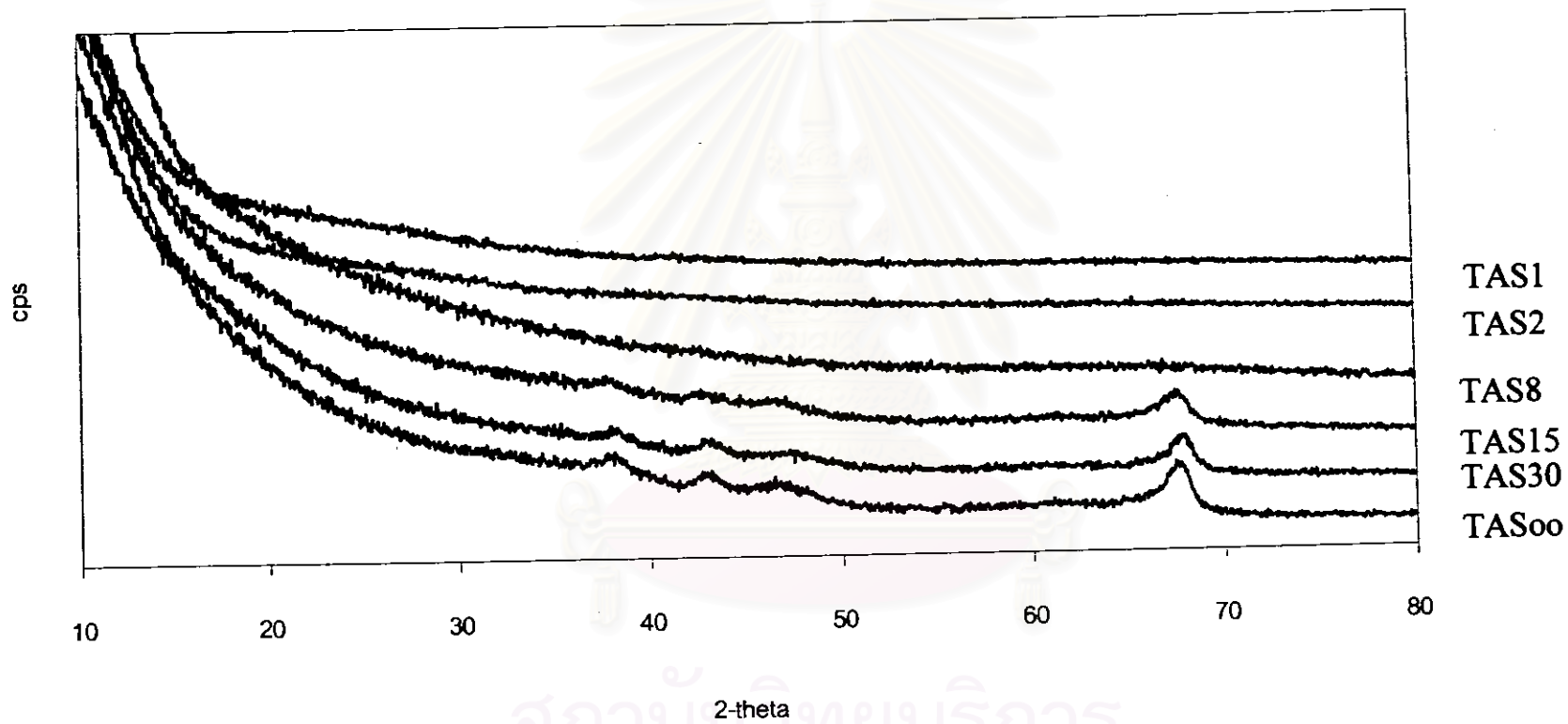


Figure 5.2a: XRD patterns of the silica-modified alumina precursor obtained by calcination at 600 °C of the precursor gels prepared in toluene

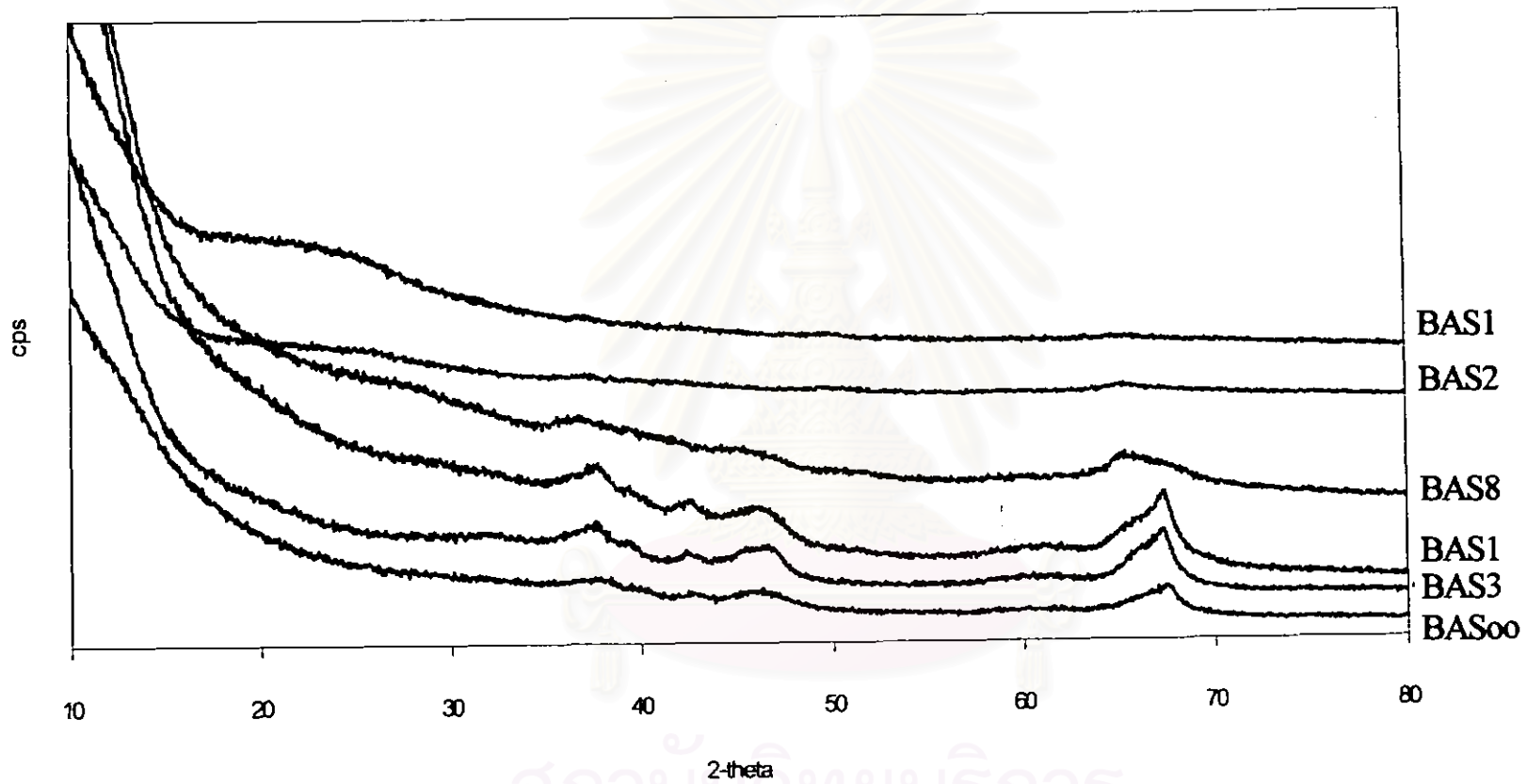


Figure 5.2b: XRD patterns of the silica-modified alumina precursor obtained by calcination at 600 °C of the precursor gels prepared in 1-butanol

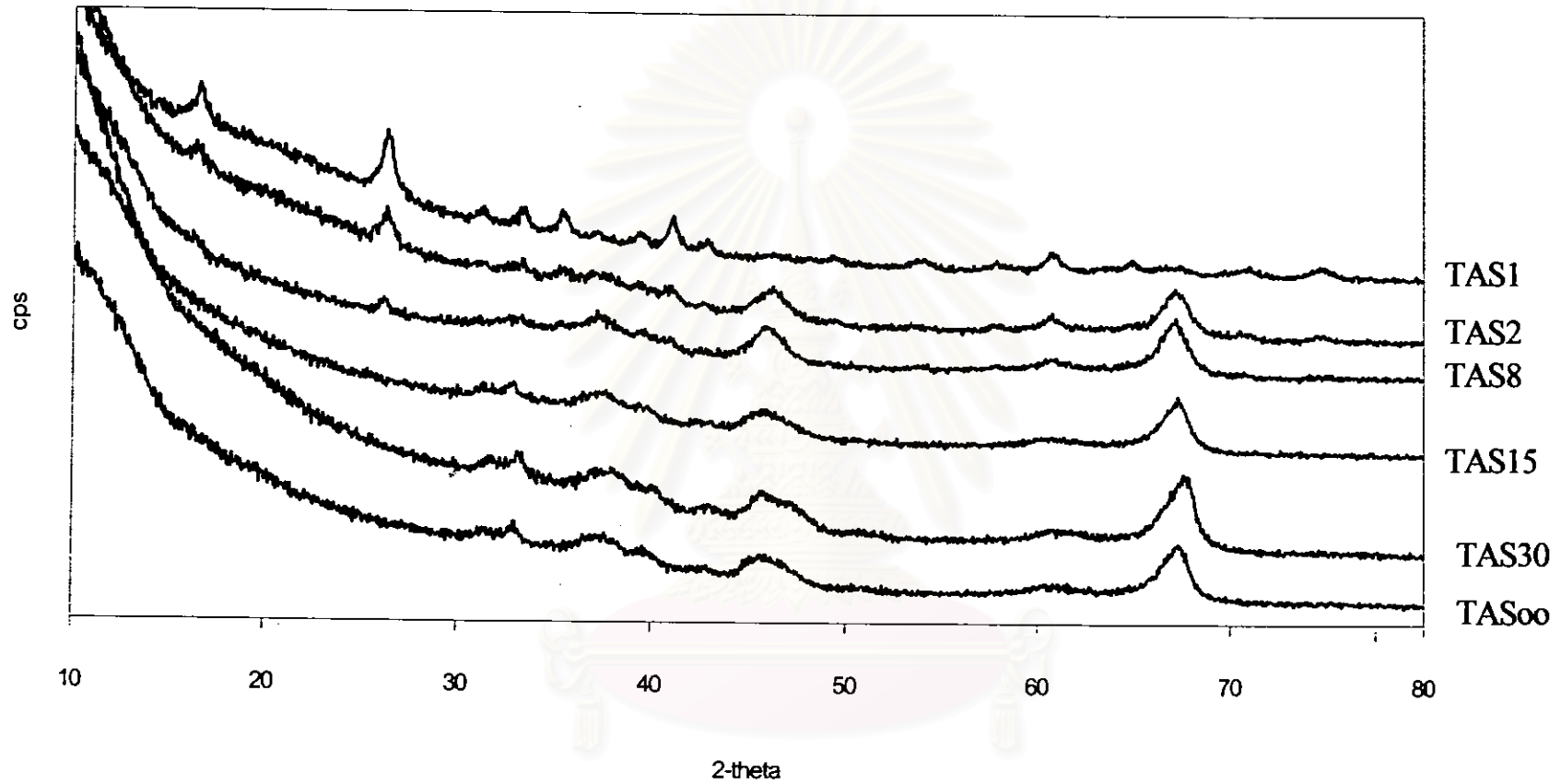


Figure 5.3a: XRD patterns of the silica-modified alumina precursor obtained by calcination at 1000 °C of the precursor gels prepared in toluene

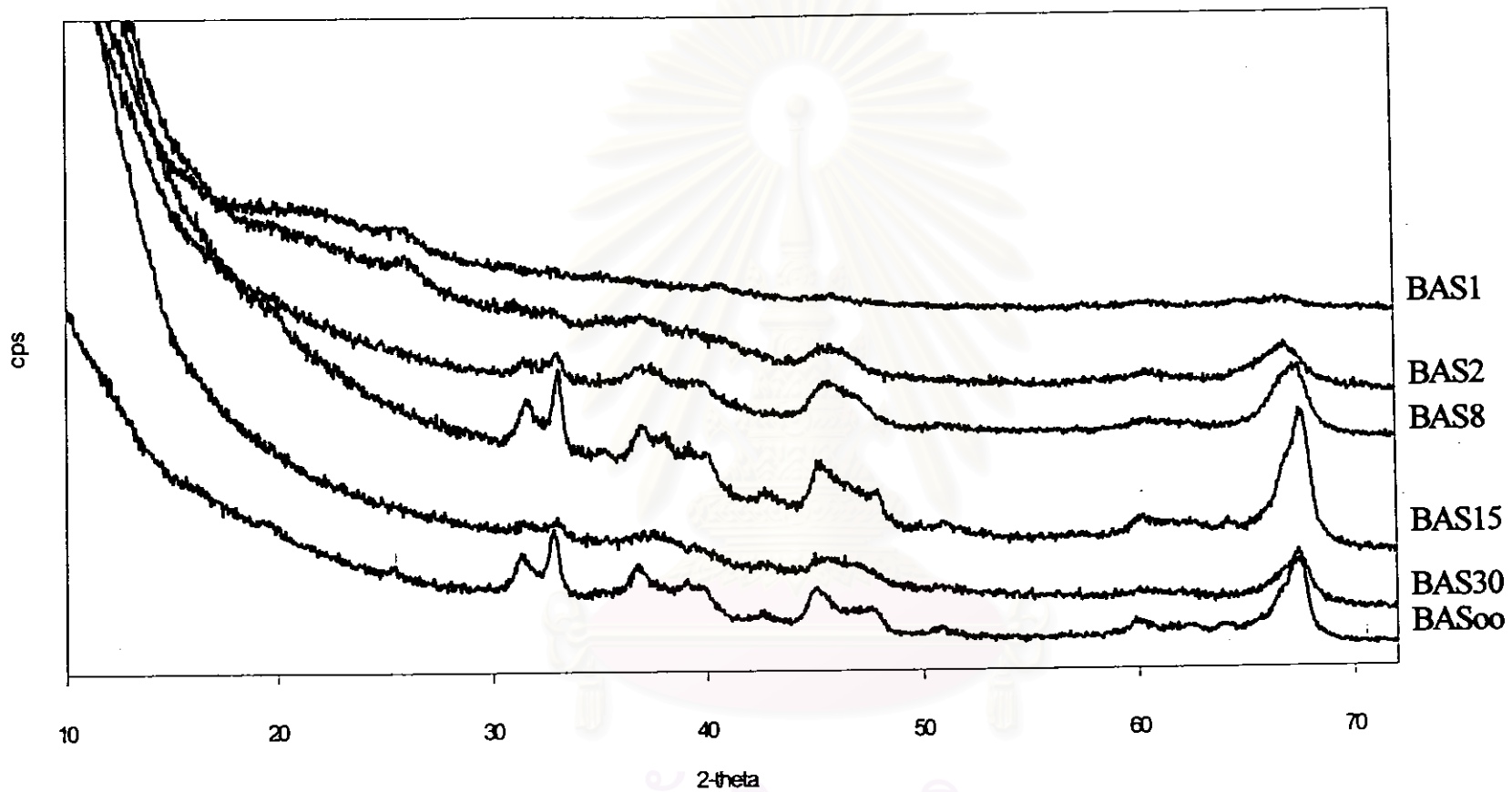


Figure 5.3b: XRD patterns of the silica-modified alumina precursor obtained by calcination at 1000 °C of the precursor gels prepared in 1-butanol

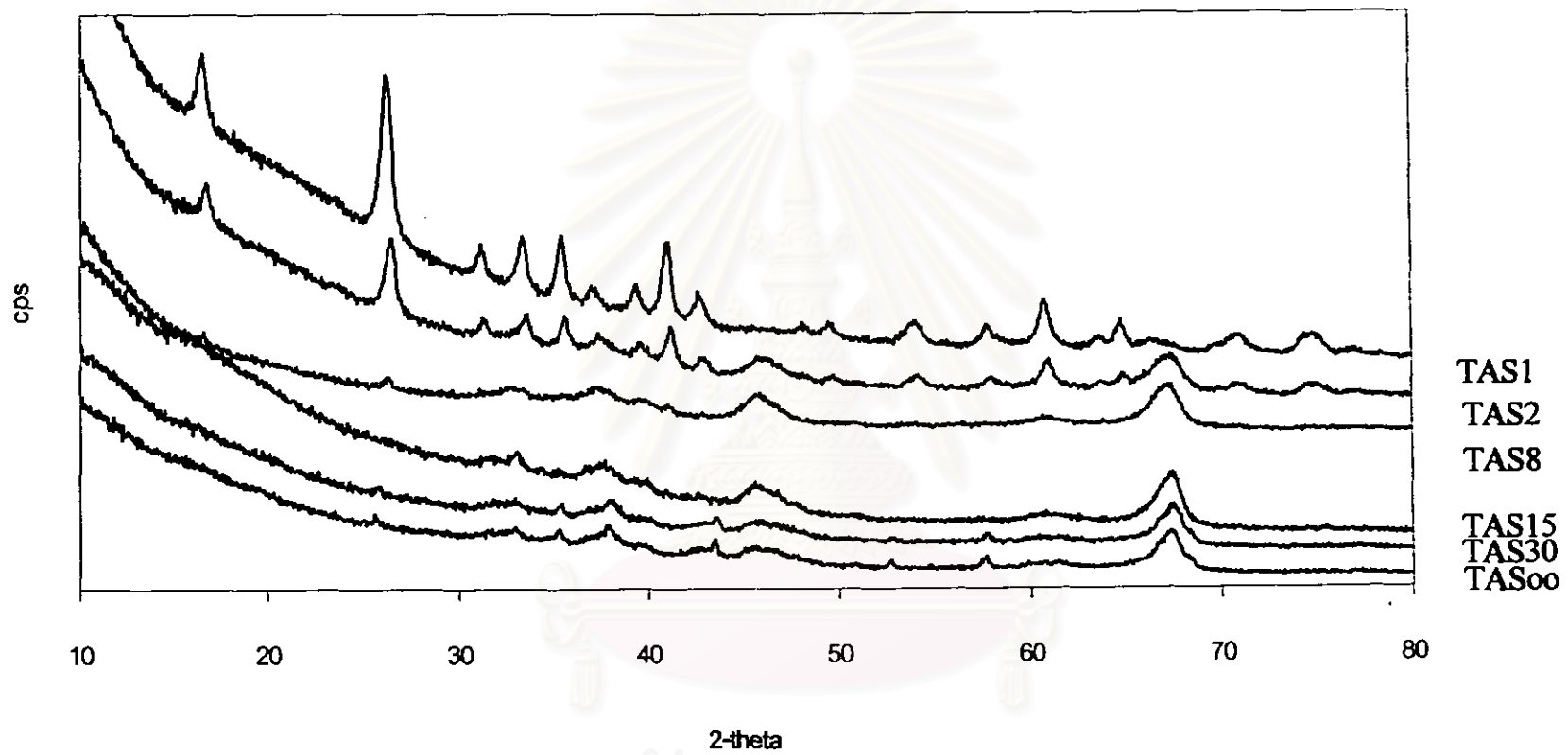


Figure 5.4a: XRD patterns of the silica-modified alumina precursor obtained by calcination at 1150 °C of the precursor gels prepared in toluene

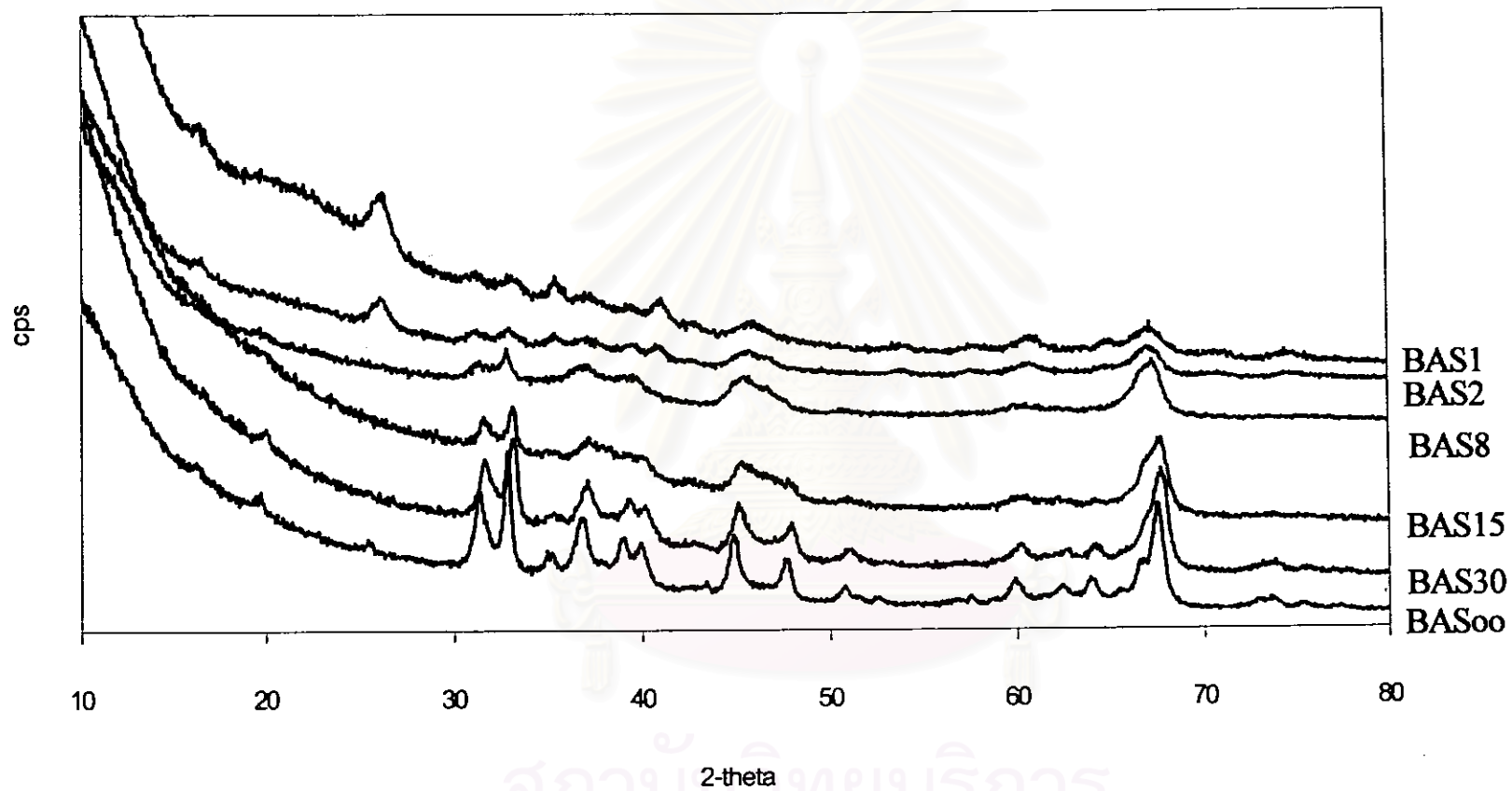


Figure 5.4b: XRD patterns of the silica-modified alumina precursor obtained by calcination at 1150 °C of the precursor gels prepared in 1-butanol

(3). Determination of functional groups of silica-modified alumina

IR is a technique, which can identify the functional groups of the products. The IR spectra of silica-modified alumina obtained by toluene and 1-butanol as synthesized are shown in Figure 5.5a and Figure 5.5b.

The IR spectra of the products obtained in toluene (TAS) are shown in Figure 5.5a. In the others investigation band characteristic of boehmite structure were seen at 773, 615 and 478 cm^{-1} but the products obtained in toluene had not the adsorption band indicating the boehmite layer. IR spectra of TAS1 showed the broad band at 1020 cm^{-1} . Apparently low wave number shifted of the Si-O-Si stretching vibration suggest that Si-O-Al bonds are partially formed by the reaction. While the IR spectra showed adsorption band at 3340 cm^{-1} that indicated the hydroxyl group. Suggesting that products obtained in toluene had not a layer structure of boehmite.

The IR spectra of products obtained in 1-butanol are shown in Figure 5.5b. Bands characteristics of the boehmite structure were seen at 773, 615 and 478 cm^{-1} , suggesting that BAS ∞ had the layer structure of boehmite. Bands due to the butyl groups incorporated between boehmite layers are also observed at 1400 cm^{-1} . The spectra of BAS30, BAS15 and BAS8 suggest the presence of boehmite. BAS1 and BAS2 exhibited the broad band at 1070 cm^{-1} due to stretching vibration mode of Si-O-Si bond.

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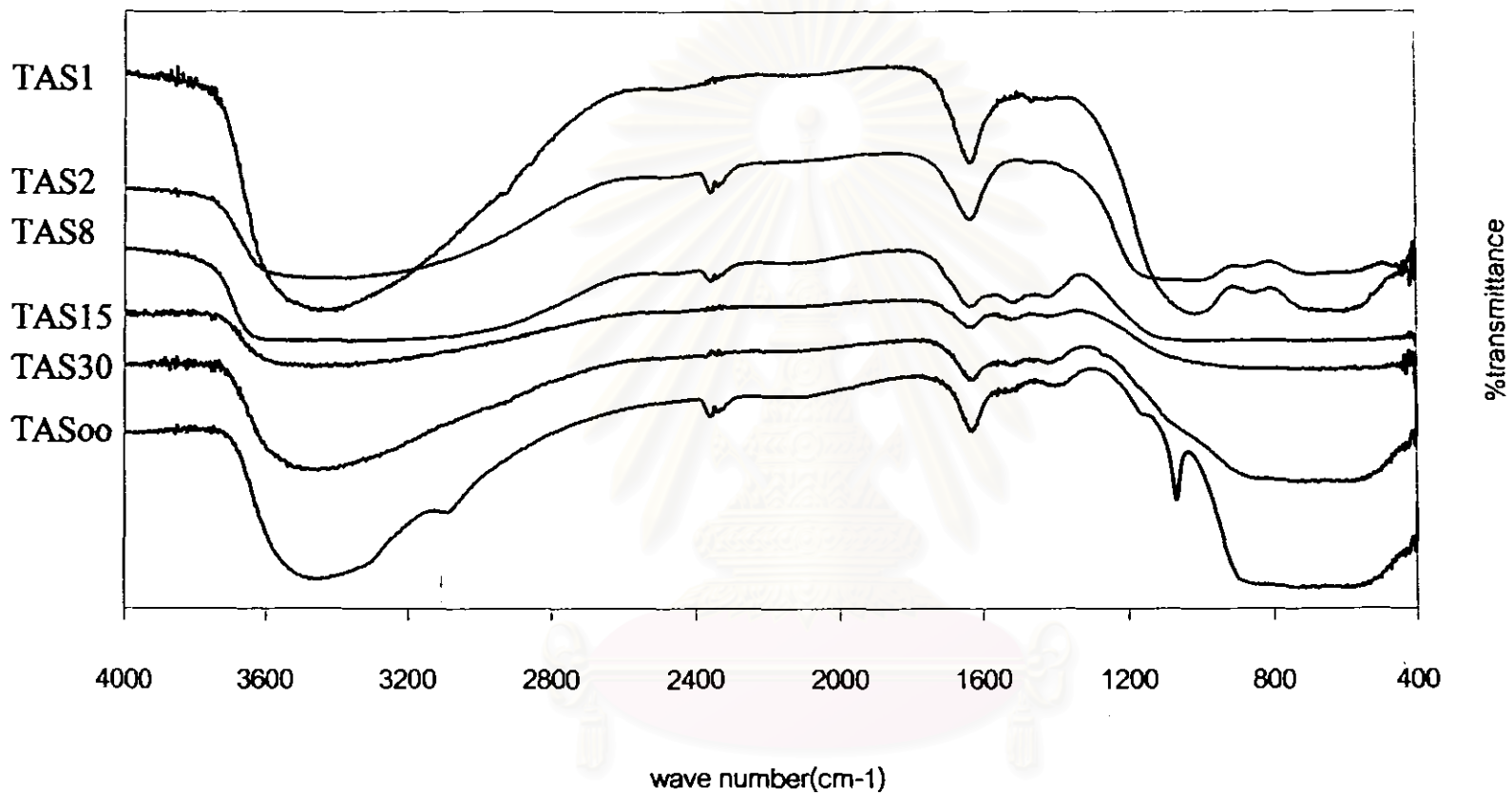


Fig 5.5a: IR spectra of precursor gels for silica-modified aluminas obtained by the reaction of AIP and TEOS in toluene with various TEOS contents

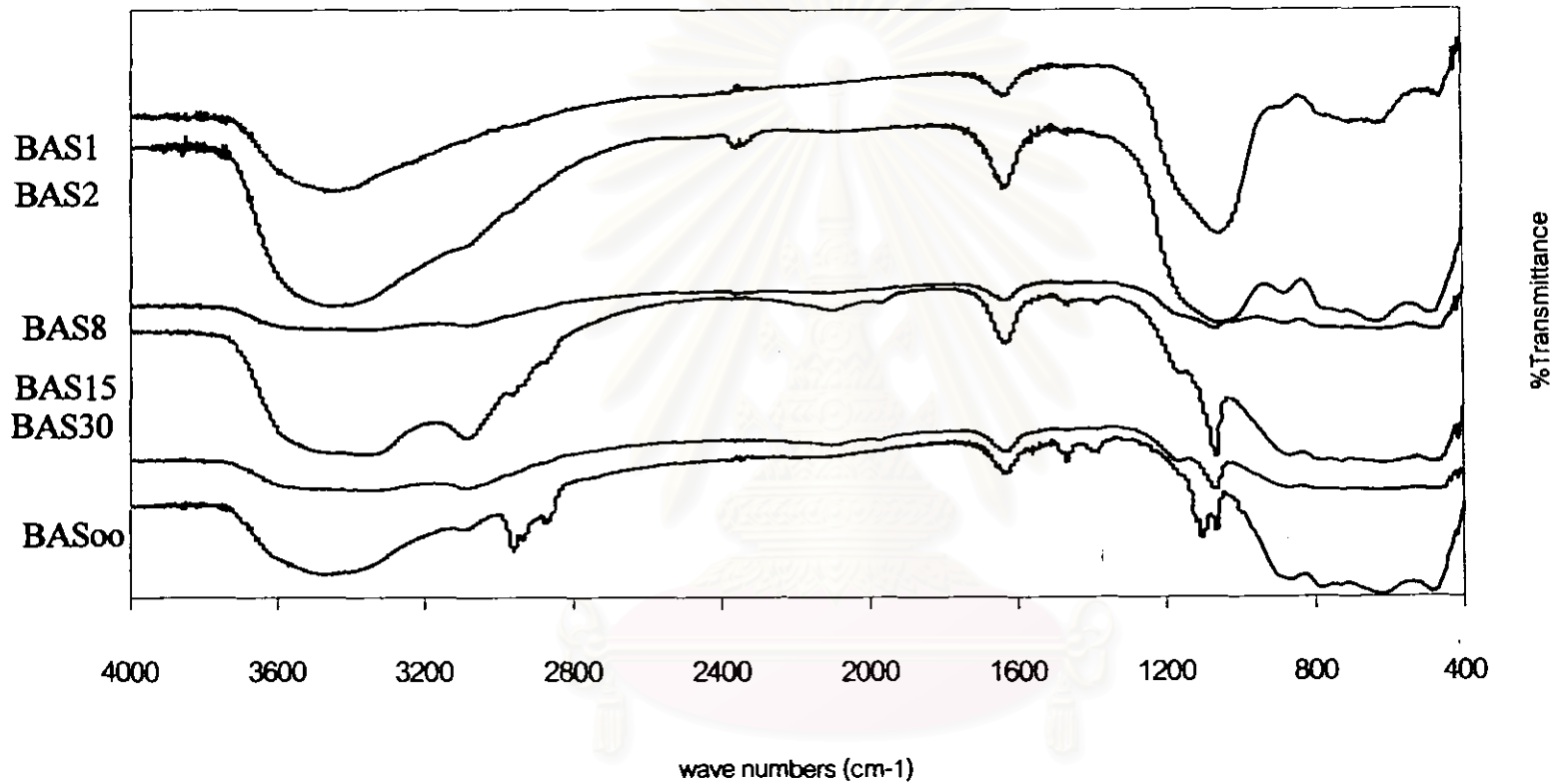


Figure 5.5b: IR spectra of precursor gels for silica-modified aluminas obtained by the reaction of AIP and TEOS in 1-butanol with various TEOS contents

(4). Determination of surface areas of silica-modified alumina

The BET surface areas of silica-modified alumina at various silicon contents and various calcination temperatures, which are determined by BET instrument, are shown in Table 5.2.

Table 5.2: The BET surface areas of silica-modified alumina at various silicon content and various calcination temperature

AIP/TEOS weight ratio	BET surface areas (m ² /g) at various calcination temperature (°C)		
	600	1000	1150
Prepared in Toluene			
TAS1	249.5	42.3	27.8
TAS2	197.9	51.2	39.4
TAS8	244.2	92.4	74.7
TAS15	157.4	111.3	101
TAS30	118.9	100	70.5
TAS ∞	105.4	88.1	65.5
Prepared in 1-butanol			
BAS1	108.4	97.1	57.1
BAS2	145.1	113.8	79.5
BAS8	210.6	190.5	168.4
BAS15	175.7	188.3	130.8
BAS30	144.8	141.1	75.3
BAS ∞	100.7	66.8	66.9
Prepared in toluene but water is added in the gap			
H3AS8	208.7	182.7	110.8
H1AS8	195.1	165.1	107

From BET surface area in Table 5.2, the product obtained in toluene. When the products were calcined at 600°C, The BET surface areas of TAS1, TAS8, TAS2, TAS15, TAS30 and TAS ∞ were high respectively. These results indicated that when TEOS contents raised in the starting materials, the BET surface area raised. It can be explained by XRD pattern of the products. TAS1 had highest surface area because phase of the products was amorphous. But BET surface area of TAS2 was lower than TAS8 because TAS2 was going to change phase. Suggesting that at 600°C the BET surface areas of the products were very effected by the presence of amounts of TEOS in the starting mixtures. When the products were calcined at 1000°C and 1150°C. TAS15 showed the highest surface areas, which is closely connected with the fact that the product maintained the χ -alumina phase even after calcination at 1150 °C. For the samples TAS1 and TAS2, the surface areas drastically decreased by calcination at high temperature, this result seem to be due to the crystallization of mullite phase at relatively low temperature.

From Table 5.2, The BET surface areas silica-modified aluminas obtained in 1-butanol were measured. When the products were calcined at various temperatures, BAS8 had highest surface area in every calcination temperature. Because XRD pattern of BAS8 phase showed the more stable than others silica-modified aluminas that calcined at same temperature and the product phase was spinel alumina that had highest surface area of transition alumina.

BET surface areas of the calcination silica-modified aluminas are shown in Table5.2. With the increase of the α -transformation temperature, the BET surface area of the silica-modified aluminas increased. The silica-modified aluminas with the weight ratio of 8 and 15 had markedly high surface area. The effect of the composition of starting materials (AIP/TEOS weight ratio) on the BET surface areas at various temperatures are shown in Figure 5.6.

Figure 5.6a : The BET surface areas of silica-modified aluminas prepared in toluene at every calcination temperature

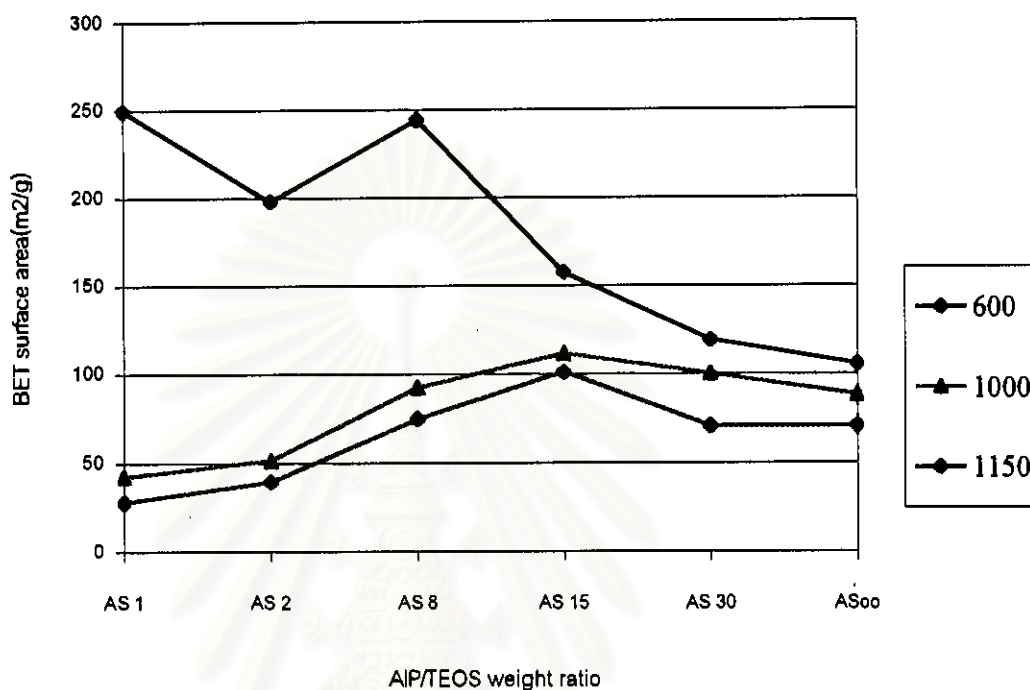
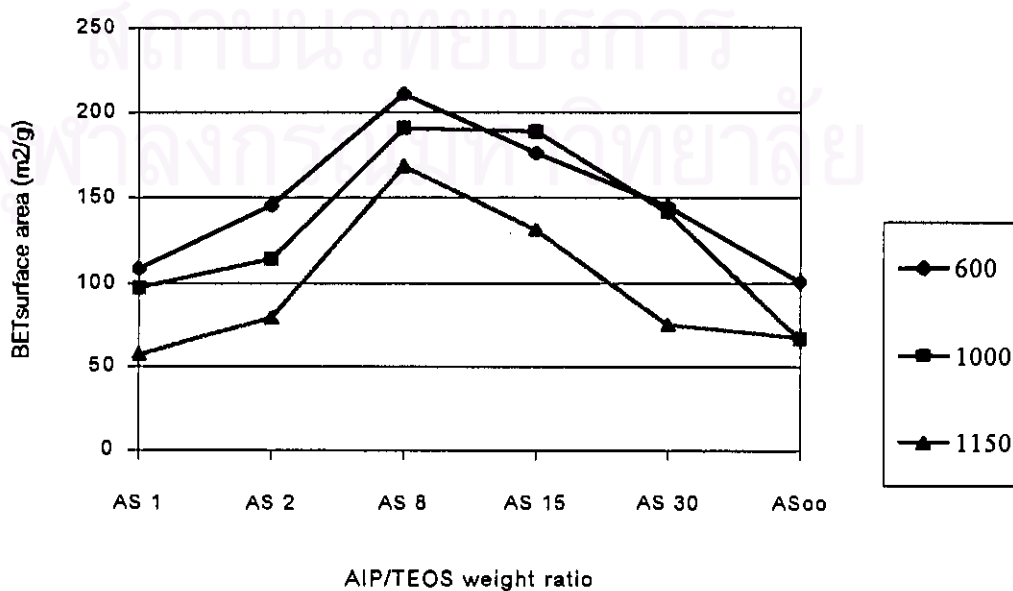


Figure 5.6b : The BET surface areas of silica-modified aluminas prepared in 1-butanol at every calcination temperature



(5). Morphology of silica-modified aluminas

TEM is a technique, which can present the morphology of the silica-modified aluminas. The TEM images of silica-modified alumina obtained by toluene and 1-butanol are shown in Figure 5.7 and Figure 5.8.

The particle shape of alumina and silica-modified alumina obtained in toluene calcined at 600°C was spherical particles. But the particle shape of alumina and silica-modified alumina obtained in 1-butanol and calcination at same temperature had thin wrinkle sheets and some spherical particles. As for BAS1(600), the thin wrinkled sheets were observed but these sheets were attached by a large number of spherical particles.

When silica-modified aluminas were calcined at 1150°C, the particle size of silica-modified aluminas obtained in toluene increased. And the wrinkle sheets of the product prepared in 1-butanol decreased.

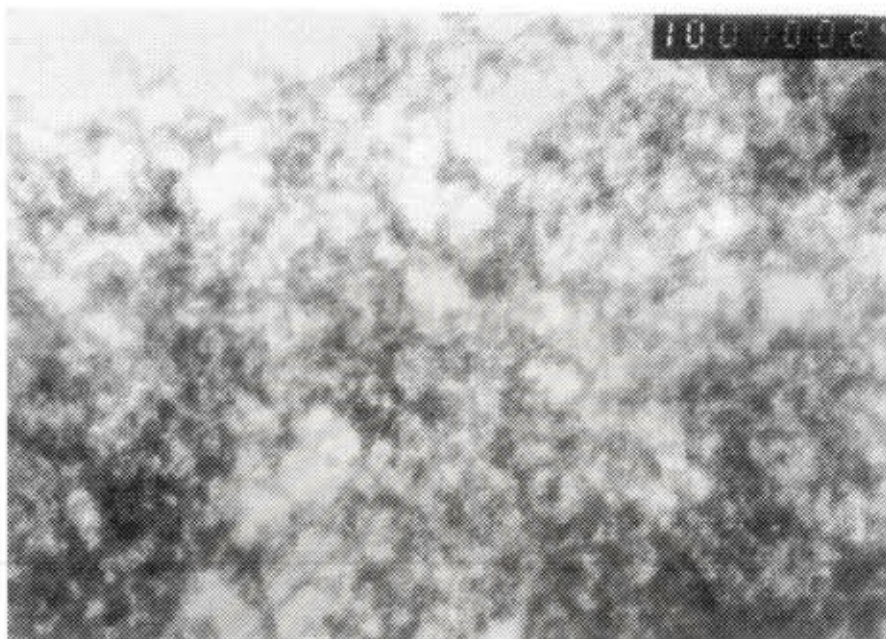


Figure 5.7a : TEM image of TAS8(600)

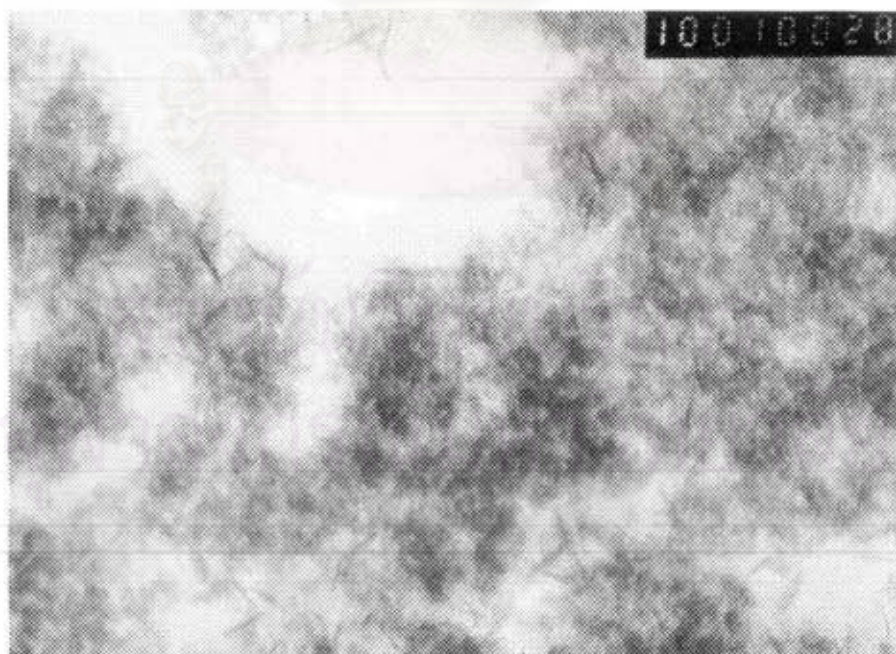


Figure 5.7b : TEM image of TAS ∞ (600)

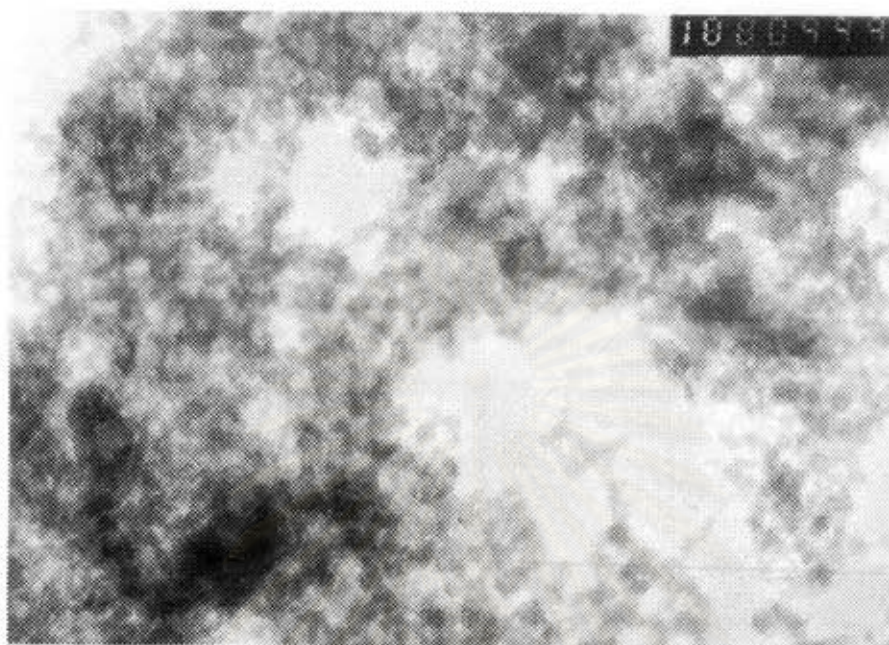


Figure 5.7c : TEM image of TAS8(1150)

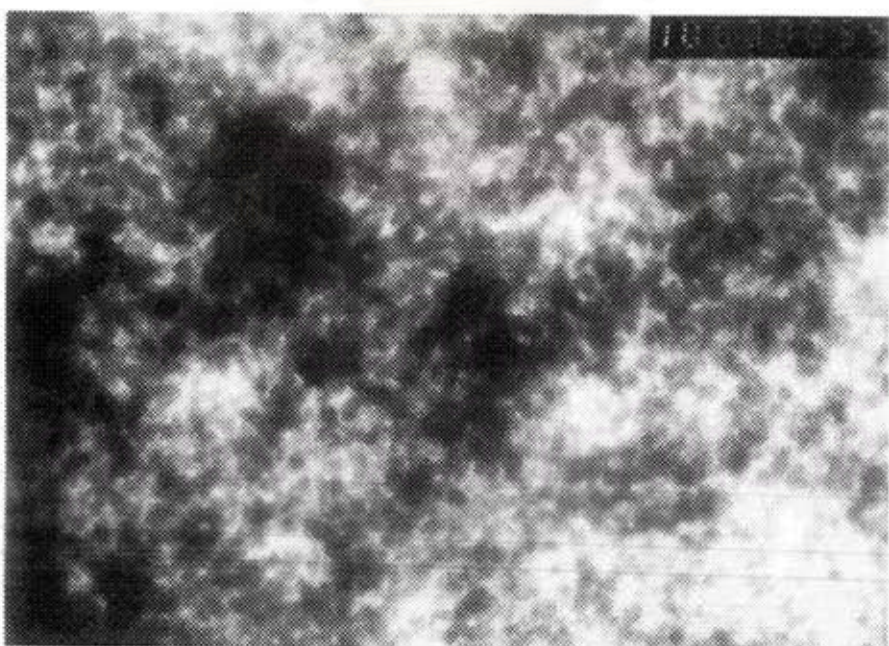


Figure 5.7d : TEM image of TAS ∞ (1150)

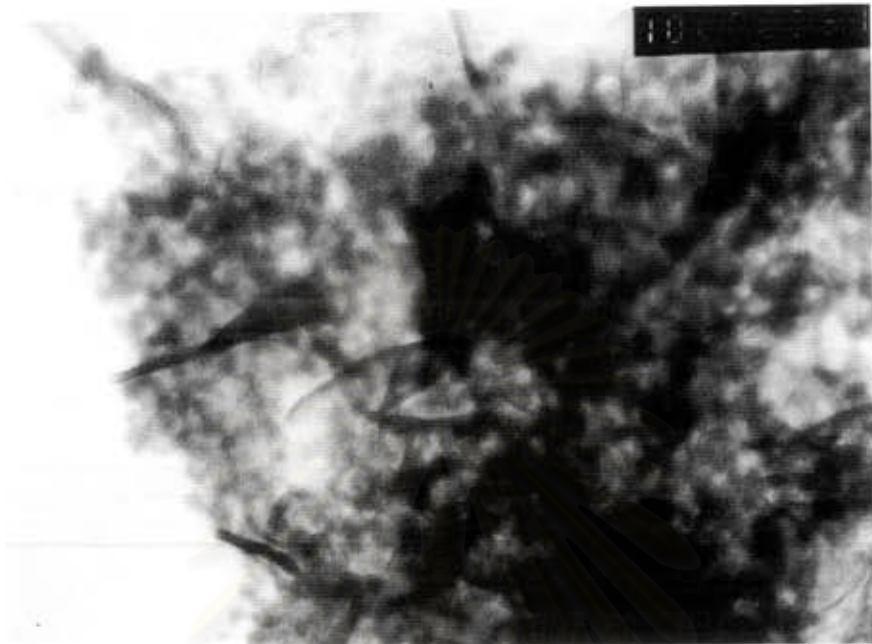


Figure 5.8a : TEM image of BAS1(600)

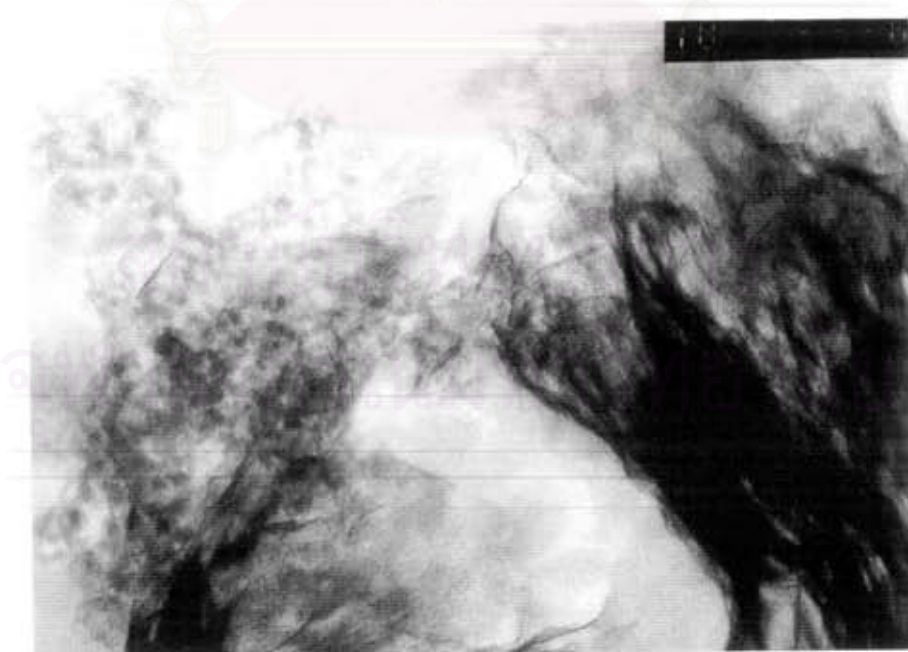


Figure 5.8b : TEM image of BAS8(600)

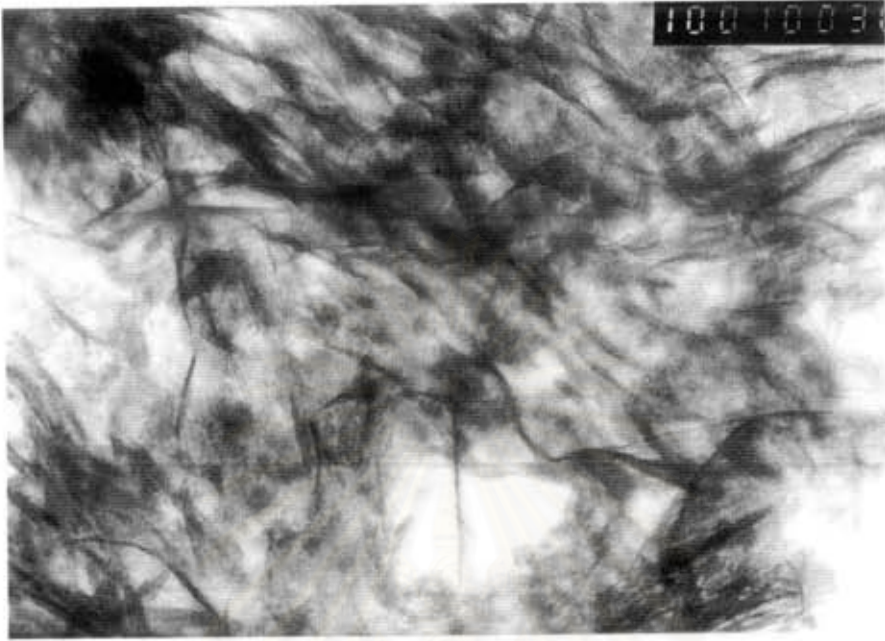


Figure 5.8c : TEM image of $BAS_{\infty}(600)$



Figure 5.8d : TEM image of $BAS_1(1150)$

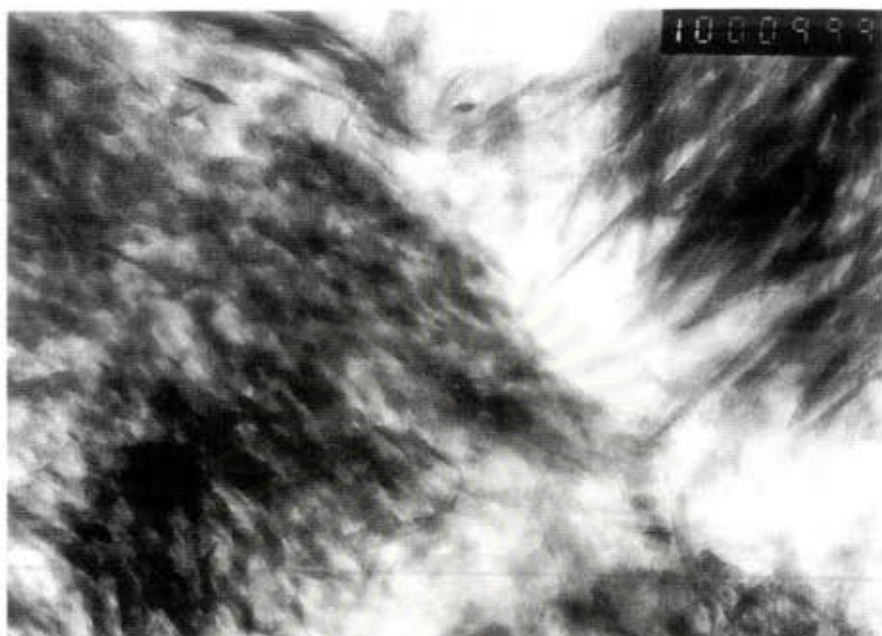


Figure 5.8e : TEM image of BAS8(1150)

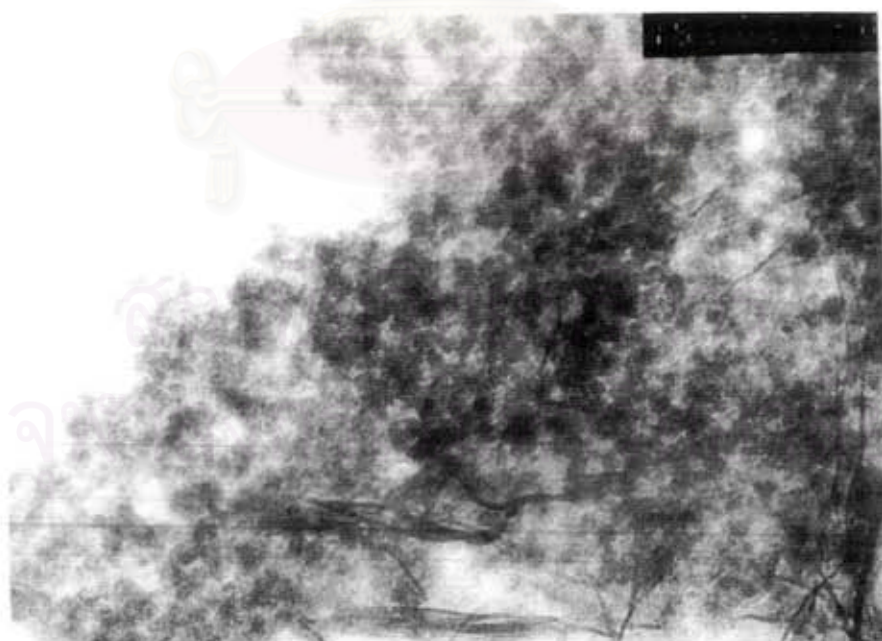


Figure 5.8f : TEM image of BAS ∞ (1150)

5.2 Testing the mechanism of one pot synthesis

In the third preparation using to compare with another methods, the product having AIP/TEOS weight ratio of 8 was prepared in toluene and some water was added in the gap between the beaker and the autoclave wall. The product was colorless powder. When structure of the product was measured by XRD, the XRD pattern of this product was similar to BAS8. When silica-modified aluminas were calcined at various temperatures. The XRD patterns showing the same XRD patterns between BAS8 and HAS8 at every calcination temperatures. The XRD patterns are shown in Figure 5.9.

IR spectra of the products using to compare with BAS8 are shown in Figure 5.10. Band characteristics of boehmite structure were seen at 773, 615, 478 cm^{-1} . Suggesting this result was as similar to BAS8.

TEM images of the products are shown in Figure 5.11. The particle shape was the mixture of some wrinkle sheets and the spherical particles similar to BAS8. But the wrinkle sheets of HAS8 were shorter and less than BAS8.

The BET surface areas of products are summarized in Table 5.2, H1AS8 and H3AS8 had larger surface area than TAS8 at high calcination temperature. The results from XRD, IR and BET suggested that the mechanism of reaction and comparison of the results between H1AS8 and H3AS8 with BAS8 suggests these reactions took place by the same reaction mechanism was different from the other two reactions in toluene.

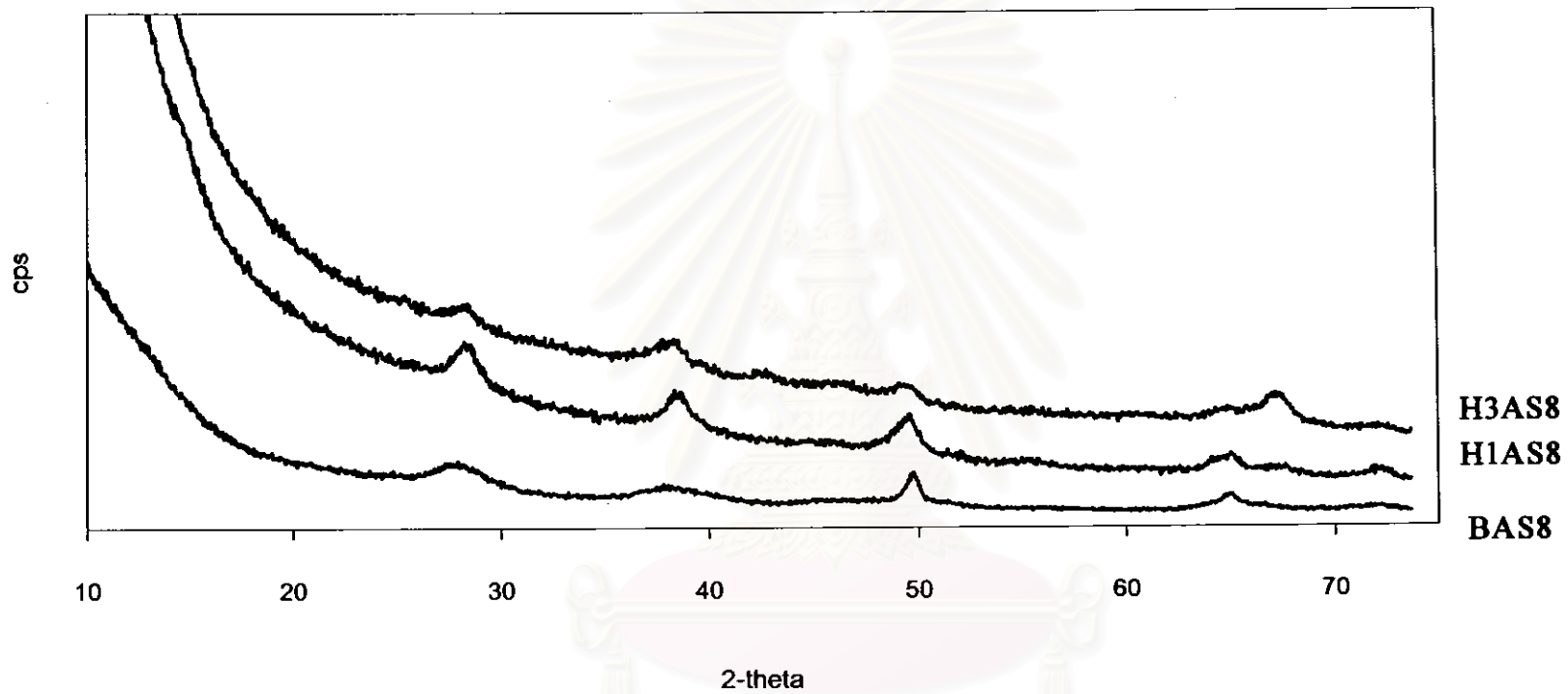


Fig 5.9a : XRD patterns of precursor gels obtained in 1-butanol and toluene, which the addition of water in the gap

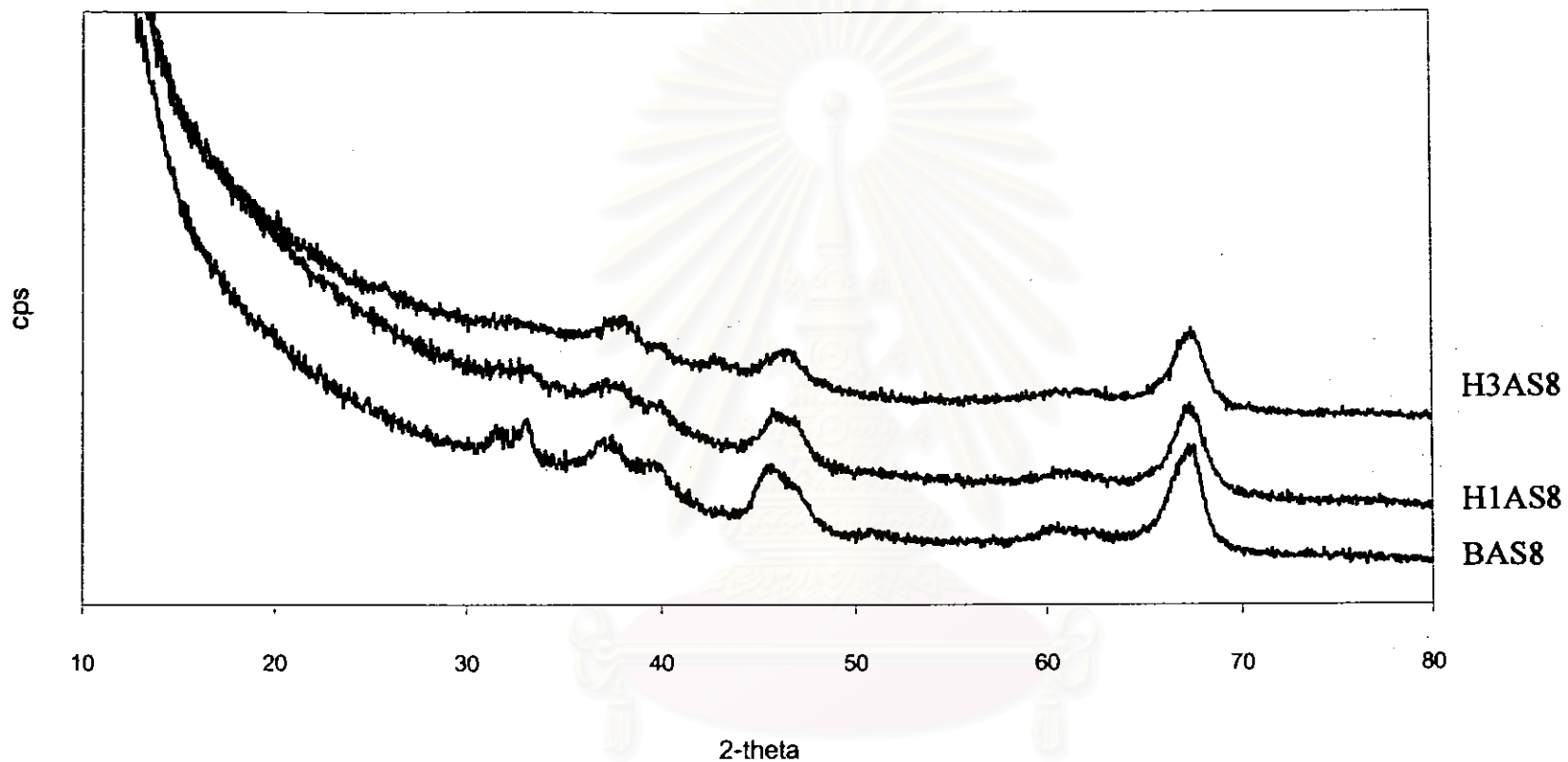


Fig 5.9b: XRD patterns of precursor gels obtained in 1-butanol and toluene, which the addition of water in the gap at calcination temperature of 1000 °C

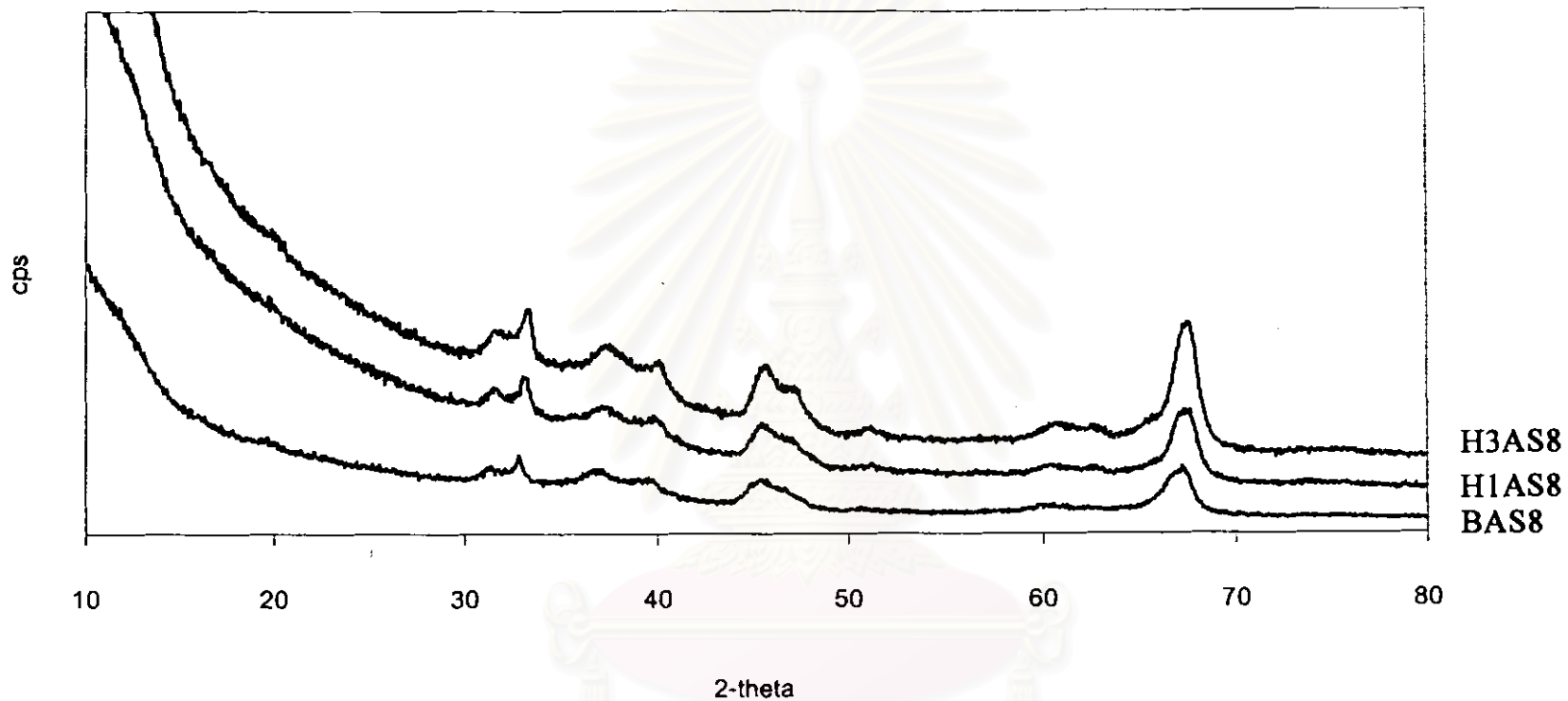


Fig 5.9c: XRD patterns of precursor gels obtained in 1-butanol and toluene, which the addition of water in the gap at calcination temperature of 1150 °C

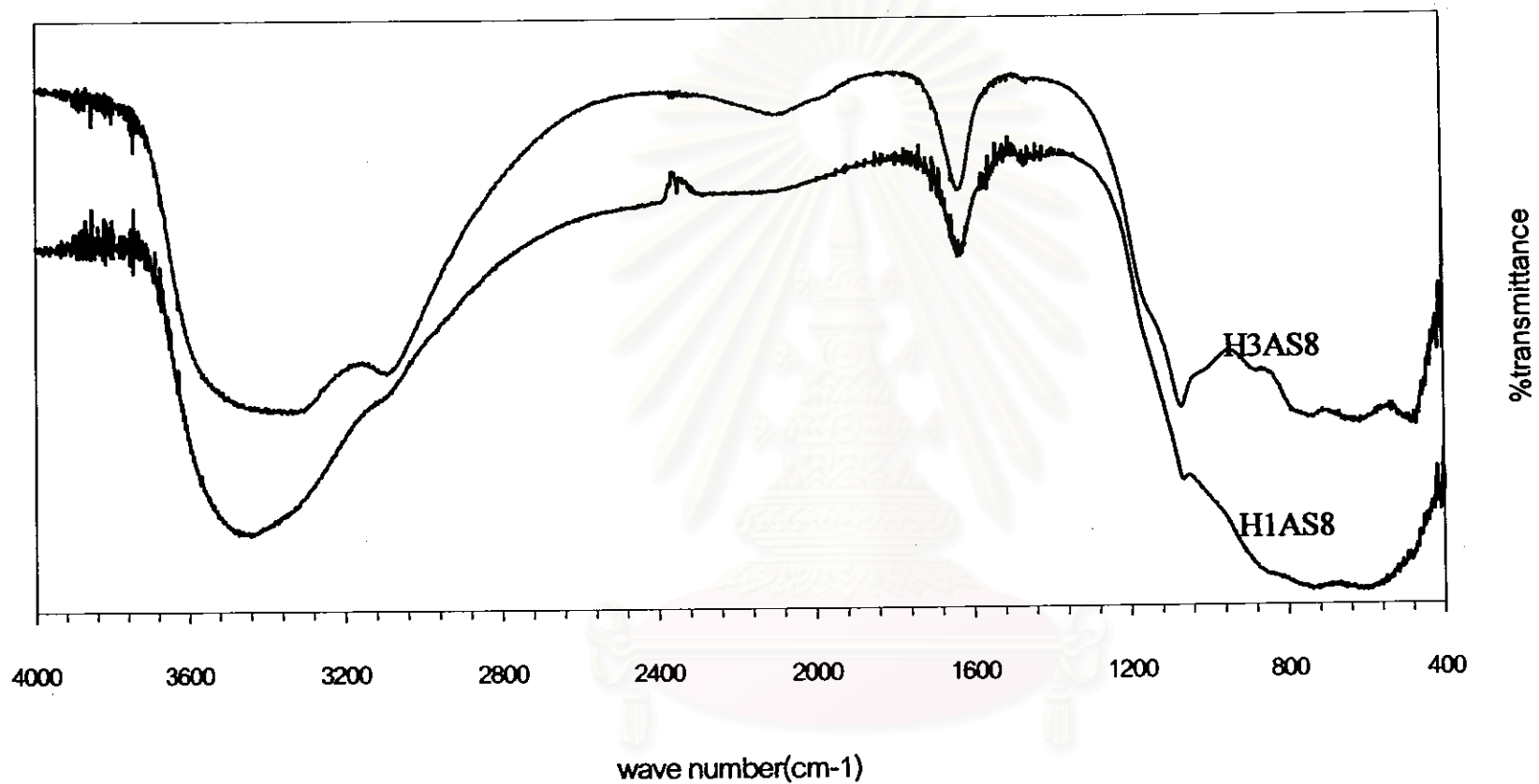


Fig 5.10 : IR spectra of the products obtained in toluene with the addition of water in the gap, between the beaker and autoclave wall

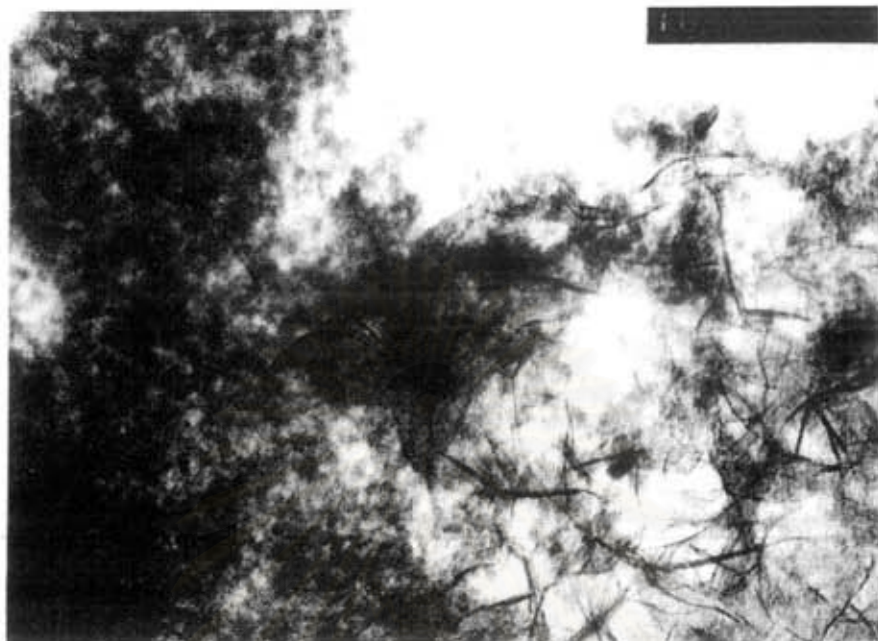


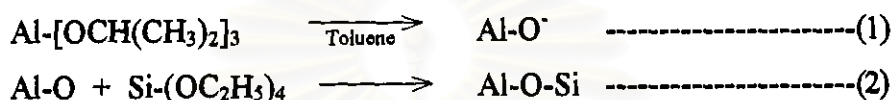
Figure 5.11a : TEM image of H3AS8(600)



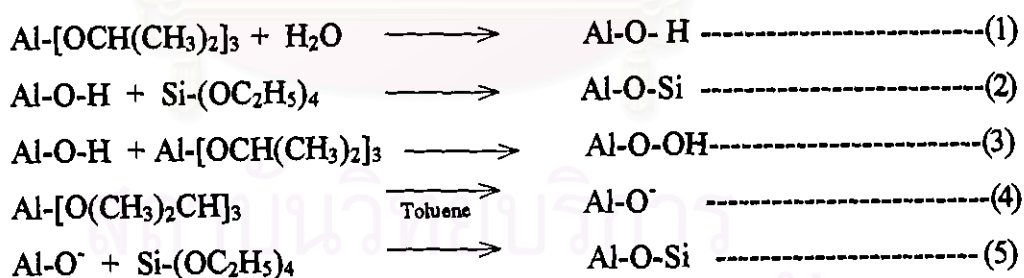
Figure 5.11b : TEM image of H3AS8(1150)

5.2 Discussion

Reaction in toluene occurred by thermal decomposition of aluminum isopropoxide. In the first step aluminum isopropoxide was decomposed yielded Al-O^- and $(\text{CH}_3)_2\text{CH}^+$ and the second step nucleophilic attack of Al-O^- on tetraethyl orthosilicate or another AIP molecule took place yield the Al-O-Si or the Al-O-Al . The lattice finally gave χ -alumina.

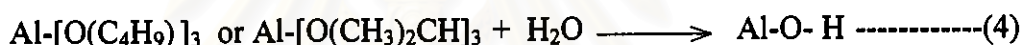
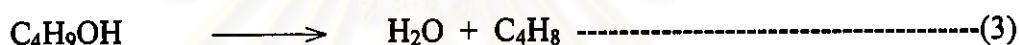
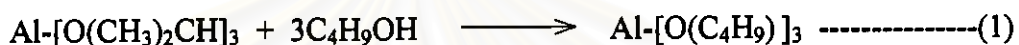


When small amounts of water was added in the gap between the beaker and the autoclave wall, the mechanism was changed. When the reaction temperature was raised, water in the gap was evaporated and dissolved in toluene in the beaker. In the second step aluminum isopropoxide was hydrolyzed yielding Al-O-H and isopropanol. Al-O-H would react with other AIP molecules finally yielded pseudoboehmite. During the polymerization reaction, the alumina species might react with TEOS remaining the silicon moiety between boehmite layers.



When 1-butanol was used as the solvent in the reaction, AIP reacts with 1-butanol yielded aluminum butoxide. Thermal decomposition of aluminum butoxide gave the alkyl (butyl) derivative on boehmite. Because the aluminum butoxide is a primary alkoxide, thermal decomposition of this compound proceeds much slowly than AIP. On the other hand, 1-butanol can be dehydrated to give water which then hydrolyzes aluminum isopropoxide or butoxide yielding Al-O-H and isopropanol or butanol. Al-O-H finally yields pseudoboehmite. Since direct decomposition of

aluminum alkoxide proceeds slowly, a part of reaction took place by this reaction sequence. In the presence of TEOS, Al-O-H species or Al-O⁻ species formed by thermal decomposition of aluminum alkoxide attacks TEOS yielding Al-O-Si bond. It's well known silica-alumina has strong acidity and therefore the products also has strong acidity. Once a small amount of product having Al-O-Si bond is formed, surface acidity of the products dehydrates the solvent, 1-butanol, yielding water, which then hydrolyzes aluminum alkoxide yielding pseudoboehmite. Therefore addition of a small amount of TEOS in the starting mixture completely altered the reaction sequence.



From TEM data, the spherical particle products were observed in products prepared in toluene. Indicating that these products occurred by thermal decomposition of aluminum alkoxide in toluene. In the other hand, the wrinkle sheets particles shape was occurred by the hydrolysis of aluminum alkoxide. Therefore the two type of products shape were observed in product preparing in 1-butanol and toluene adding water in the gap between the beaker and the autoclave wall. These results supported the upper mechanism. Indicating that the thermal decomposition of AIP and the hydrolysis of aluminum alkoxide occurred in both of in 1-butanol and toluene adding water in the gap between the beaker and the autoclave wall.

From BET surface areas of the products shown in Table1, the products obtained in toluene and the presence of various amounts of water in the gap between the autoclave wall and the beaker had different surface areas that indicated the amount of water had the effect on the reaction. However the surface areas were far lower than

those of the product obtained in 1-Butanol, The results indicated that the reaction in toluene having water in the gap had 2 simultaneous reaction, i.e. the hydrolysis of AIP and thermal decomposition of AIP which occurred at the same temperature. The higher thermal stability of the products obtained in 1-butanol, suggested that the hydrolysis of AIP was the main reaction.

Iler (1964) suggested that silica reacts with alumina to form an extremely viscous glassy phase, which coats the alumina surface and retards the migration of alumina. . Yoldas (1976) prepared silica-modified alumina by partial hydrolysis of a mixture of aluminum sec-butoxide and TEOS. The silica-modified alumina prepared by this method showed high α -alumina crystallization temperature. He explained that silica goes into certain sites in the structure of alumina, causing no disturbance in the lattice, and explained the existence of an optimal silica contents for the stabilization of the products by saturation of the sites. Gani and Mcpherson (1977) prepared silica-modified alumina by plasma decomposition of aluminum and silicon chlorides and found α -alumina crystallization temperature was 1500°C. Since the powders were formed by rapid cooling from the melt, aluminum and silicon were distributed homogeneously in atomic scale. He explained that silicon atoms are strongly bound within the tetrahedral sites of the spinel structure, which retards the rearrangement of oxygen atom from face centered-cubic closet packing of alumina. However the powders had low surface area, and therefore this products is not suitable for the catalyst or catalyst support. Johnson (1990) explained the stabilizing effect of silica-modified alumina by the reduction of the number of surface hydroxyl because of the formation of Al-O-Si bounds from hydroxyl. Beguin (1991) explained that a silica layer grafted to alumina is able to fill the anionic vacancies of alumina. Inoue et al. (1995) prepared silica-modified alumina in 1,4-butanediol. They found high thermal stability of the product and explained that incorporation of silicon atoms in the spinel structure of alumina allows one to substitute surface hydroxyls or anion vacancies with oxides ions or hydroxyls to maintain charge neutrality of the particles, which then increases the energy required to nucleation of α -alumina at the surface of particles.

Because homogeneous incorporation of silicon atoms in the structure of alumina elevated the α -alumina crystallization temperature, silicon atoms must be incorporated in the spinel structure. However a limited number of silicon atoms can be accommodated in the spinel structure. When large excess of TEOS was allowed to react with AIP, TEOS seem to be decomposed by a different mechanism. The decomposition of TEOS alone gave amorphous silica. TAS1, TAS2 was calcined at 1150°C. The mullite phase was found.

That was the reason why the product obtained in each solvent had not the same maximum point of AIP/TEOS weight ratio. The products obtained in 1-butanol, BAS8 had a highest surface area at every calcination temperature include at 1150. In toluene, the product had AIP/TEOS weight ratio 15 had a highest surface area at 1150°C. Because of the difference structure of the products, χ -alumina for TAS and boehmite structure for BAS, thus the highest thermal stability of each product was obtained at difference AIP/TEOS weight ratio. BAS8 and TAS15 were found to have highest thermal stability. The XRD patterns of TAS8(1000) and TAS8(1150) had peak that showed the presence of mullite phase while these peaks were not observed in BAS8 at any calcination temperature. This means that for BAS, silicon atoms could bond with aluminum atoms in structure of boehmite more than products obtained in toluene, TAS. It is interesting to note that when the water was added in the gap between autoclave wall and beaker, the peaks of mullite phase were not observed at any calcination temperature in HAS samples. The results were also confirmed when using the difference amounts of water. The results of, which were similar to those, obtained from the products prepared in 1-butanol, BAS, which silicon atoms could readily bond with aluminum atoms in boehmite structure. Therefore, the AIP might also be hydrolyzed with water to boehmite, leading to the better bonding between Si and Al for the formation of spinel phase.

From TEM data, the wrinkle sheets of the product obtained when the system had some water or thermal decomposition of primary alkoxide. When the solvent gave more water, the amounts of wrinkle sheets increased. This result suggested that if the thermal decomposition of AIP decreased the amounts of wrinkle sheets

increased. From Table 5.2, the BET surface areas and the thermal stability increased with the increasing of wrinkle sheets because the part researchers reported that the α -transformation was occurred at the connection of the particle. The spherical particles had many connections of the particles. Therefore the wrinkle sheets could decrease the connections between the particles and the thermal stability of the products increased.



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