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One Pot Solvothermal Synthesis of Thermally Stable, Porous Silica-Modified Alumina Powders by Supercritical Removal of Organic Solvents

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Abstract

Mixtures of alumina isopropoxide (AIP) and tetraethyl orthosilicate (TEOS) in each organic solvent (toluene, 1-butanol and toluene + water in the gap) were set in an autoclave and heated at 300°C for 2 h. The fluid phase was removed above the supercritical temperature. The products were calcined in air to yield silica-modified aluminas. These silica-modified aluminas had high thermal stabilities and maintained large surface areas at high temperatures. For example, the product prepared from mixture of AIP and TEOS with Al/Si = 8 in 1-butanol had a surface area of 169 m^2/g after calcination at 1150°C. The surface area and thermal stability of products depended on the reaction mechanism operated in each solvent.

Introduction

Recently, much attention has been paid to improve the properties of catalyst at high temperatures. Transition aluminas have large surface areas with reasonable mechanical strength and are widely used as catalyst supports in industry. However, because of metastable nature of transition aluminas, they usually transform to α-alumina at around 1100°C which causes a drastic decrease in the surface area. For the purpose of increasing the thermal stability of transition aluminas, the effect of dopants has been investigated and partial success was achieved by incorporation of ThO2, ZrO_2, SiO_2, etc., in to the alumina matrix.

Iler (1964) found that the addition of silicic acid to fibrillar colloidal boehmite increased the thermal stability of the resultant alumina. Yoldas (1976) examined the thermal stabilities of silica-modified aluminas prepared by a sol-gel method and reported that the alumina doped with 6% silica had the maximum temperature (1380°C) for α-alumina transformation. Murrell and Dispenziere (1988) reported that the alumina doped with 5%

silica by reaction with tetraethyl orthosilicate (TEOS) led to marked stabilization against loss of the surface area by vanadium attack at high temperatures. In other papers in this field, Johnson (1990), and Beguin, *et al.* (1991) also prepared silica-modified alumina and confirmed the increase of the thermal stability of the resultant alumina by addition of silica.

For the synthesis of inorganic materials by using organic media, Inoue, *et al.* (1988), Inoue, *et al.* (1989), and Inoue, *et al.* (1992) found that the glycothermal treatment (the use of glycol instead of water for hydrothermal treatment) of gibbsite at 250°C yielded the product having structure of boehmite with glycol moieties incorporated between the boehmite layers with the covalent bonding. Inoue, *et al.* (1988) also found that the treatment of aluminum alkoxide in various glycols at 300°C yielded the glycol derivative on boehmite. Inoue, *et al.* (1995) had prepared the silica-modified alumina by the reaction of aluminum isopropoxide (AIP) and tetraethyl orthosilicate (TEOS) in 1,4 butanediol at 300°C and found that the product with Al/Si ratio of 8 maintained large surface area even after calcination at high temperature.

Highly porous solids can be prepared by the removal of solvent from a wet gel at a temperature above the critical temperature of the solvent. In recent years, researchers have built up the strong technical background in such materials. Fanelli and Burlew (1983) found the new polymerization catalyst system comprising an aluminum compound and a transition metal compound on an alumina-based aerogel support. Armor and Carlson (1984) prepared a catalyst composition of a uniform dispersion of individual metallic palladium particles. Armor and Carlson (1989) also prepared high pore volume alumina by hydrolysis of AIP followed by supercritical removal of fluid phase. Aerogel has good properties such as high pore volume, high surface area, and high thermal stability. These properties result from this method that obviates the inherent shrinkage or structural collapse that occurs when precursor gel are conventionally dried to a solid form. Such shrinkage or are brought about by the surface tension of residual liquid trapped within the fragile gel structure.

In the present work, mixtures of AIP and TEOS were treated in 1-butanol, and toluene, and the fluid phase was separated by supercritical drying. In other words, solvothermal synthesis of oxides is combined with the supercritical drying method, which provides a convenient route for the synthesis of powders by using only one reaction vessel. The properties of products are also examined. The products are calcined at various temperatures, and then thermal stabilities of the resulting silica-modified aluminas are investigated.

Experiment

In this paper, the products were prepared by three different methods. First, the mixtures of aluminum isopropoxide (AIP, Aldrich) and tetraethyl orthosilicate (TEOS, Aldrich) were suspended in 100 ml of toluene in a beaker, and then set up in a 300 ml autoclave. In the gap between the beaker and the autoclave wall, 30 ml of toluene was added, After the autoclave was completely purged with nitrogen, the suspension was heated to 300°C at a rate of 2.3°C/min and held at this temperature for 2 h. During the reaction, the autogenous pressure gradually increased to 6-14 MPa. After the reaction, the autoclave valve was opened, and the fluid phase in the autoclave was released at that temperature condensing in a cooling coil. The condensed liquid was collected in another beaker. After the autoclave was cooled, the white powder products were obtained. For the second and the methods, the same procedures as the first one were followed except that 1-butanol and mixture of water and toluene was added instead of toluene, respectively. Amount of water was varied between 10 and 30 ml. The AIP/TEOS weight ratios of the first and second preparation methods were varied as 1, 2, 8, 15, 30, ∞ but only the AIP/TEOS weight ratio of 8 was used for the third preparation method.

A part of the product was calcined in a box furnace by heating to the desired temperature (600°C -1150°C) at a rate of 10 °C/min and holding at that temperature for 1 h, and thus silica-modified aluminas were obtained.

The reaction products will be abbreviated by T, B and H to represent the solvents that used in the reaction where toluene, 1-butanol, and mixture of water and toluene were used in the gap between the beaker and the autoclave wall, respectively. The number followed H was the amount of water used in the gap (*10ml). The abbreviation AS, means the silica-modified alumina. The number after AS is a number for the AIP/TEOS weight ratio in the reaction mixture, i.e., Al or AS∞ was the product obtained by AIP alone. When calcined samples are specified by calcination temperature in the parenthesis. For examples TAS∞(1150) and TAl (1150) means the alumina sample prepared in toluene and calcined at 1150 °C, respectively.

Characterization

Powder X-ray diffraction (XRD) was measured on a SIEMENS XRD D5000 using Cu Kα radiation, Infrared (IR) Spectra were recorded on a NICOLET FT-IR Impact 400 spectroscopy using the ex-situ IR technique. The BET surface areas were calculated by the BET-single point method on the basis of the nitrogen uptake measured at P/Po = 0.3 using a gas chromatograph. The surface areas calculated by the ordinary BET method were in good agreement with the surface areas calculated by the single-point method.

Results

The products obtained by one-pot synthesis of mixtures of AIP and TEOS in toluene were colorless powders. The XRD patterns are shown in Figure 1a. The TAS∞ exhibited the typical pattern for χ-alumina. When the amount of TEOS in the starting mixture increased, peaks due to χ-alumina became weak and TAS1, TAS2, TAS8 were amorphous. When mixtures of AIP and TEOS were allowed to react in 1-butanol, the products were colorless powders. As shown in Figure 1b, BAS∞ exhibited the typical pattern for the alkyl derivative of boehmite. This pattern was similar to that of pseudoboehmite but the peak at angles $14^{\circ}(2\theta)$ shifted to the lower angle sides. The XRD patterns of BAS30 and BAS15 suggest that these products were mixtures of χ-alumina and pseudoboehmite. With the increase of the TEOS content in the starting mixture, the peak intensities became weak and BAS1 was amorphous.

IR spectra of the products are shown in Figure 3. Band 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. The spectra of BAS30, BAS15 and BAS8 suggest the presence of boehmite. BAS1 and BAS2 exhibited the broad and at 1070 cm^{-1} due to stretching vibration mode of Si-O bonds. On the other hand products obtained in toluene had no adsorption band that indicated the boehmite layer. IR spectra of TAS1 showed the broad band at 1020 cm^{-1}. Apparently low wave number shift of the Si-O stretching vibration suggests that Si-O and Al-O bonds are partially formed by the reaction.

The products were calcined at various temperatures, and their phase transformations were determined by XRD. The XRD patterns of the products prepared in toluene and 1-butanol and calcined at 1150°C for 1h are shown as representative data in Figures 2a and 2b

The XRD patterns of TAS1(1150) and TAS2(1150) showed the presence of mullite phase together with small amounts of the spinel phase, while TAS∞(1150) and TAS30(1150) exhibited the XRD patterns due to χ-alumina together with a small amount of α-alumina. Noted that no high-temperature transformation such as θ- and η-alumina were detected. Direct transformation of a low-temperature transition alumina (χ-alumina) into α-alumina is specific character of alumina formed by thermal decomposition of aluminum alkoxide in inert organic solvent. TAS8(1150) exhibited the XRD pattern for spinel phase and mullite phase, while TAS15(1150) exhibited the XRD pattern typical for spinel phase.

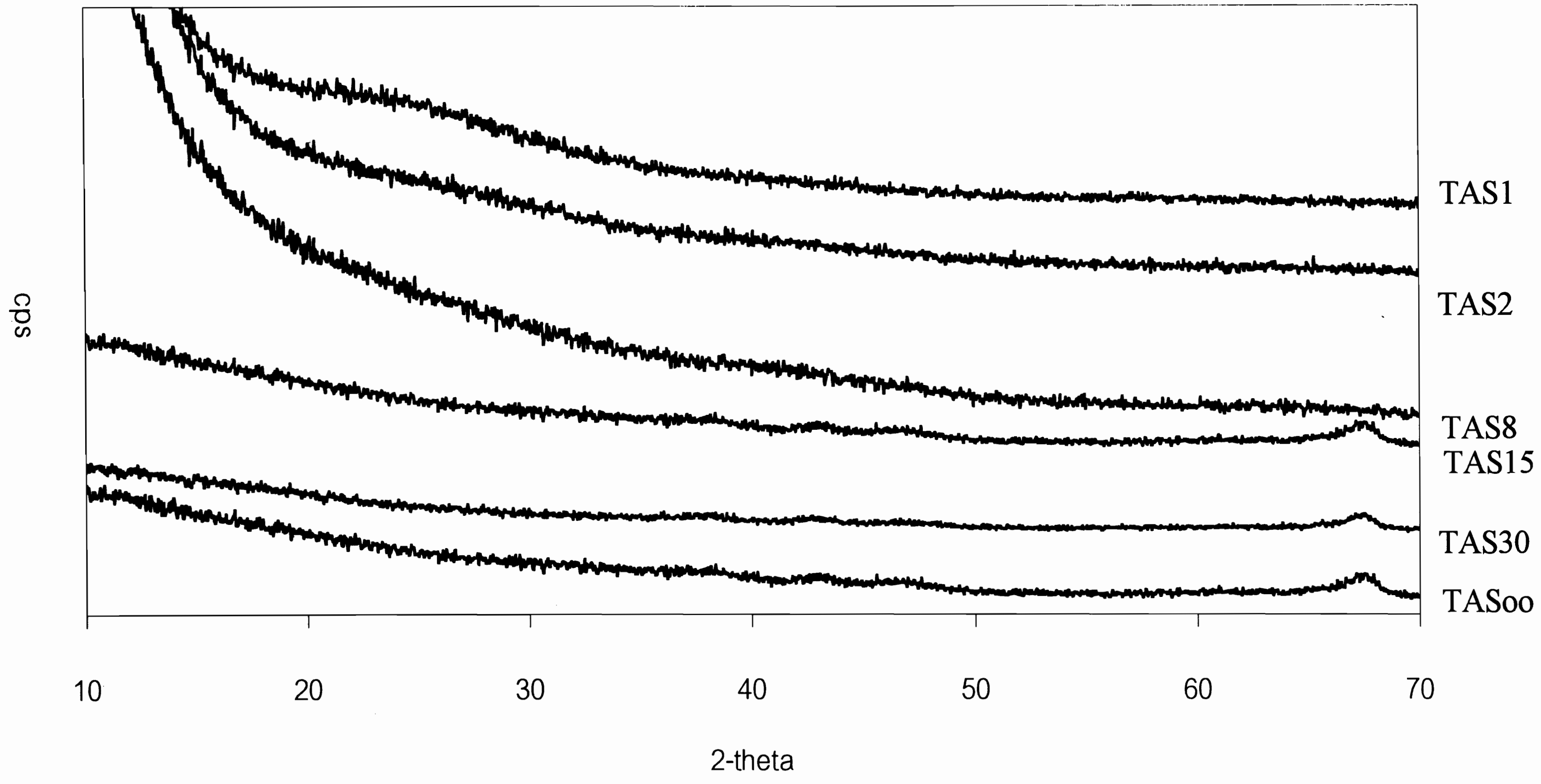

Figure 1a: XRD patterns of precursor gels obtained by the reaction of AIP and TEOS in toluene

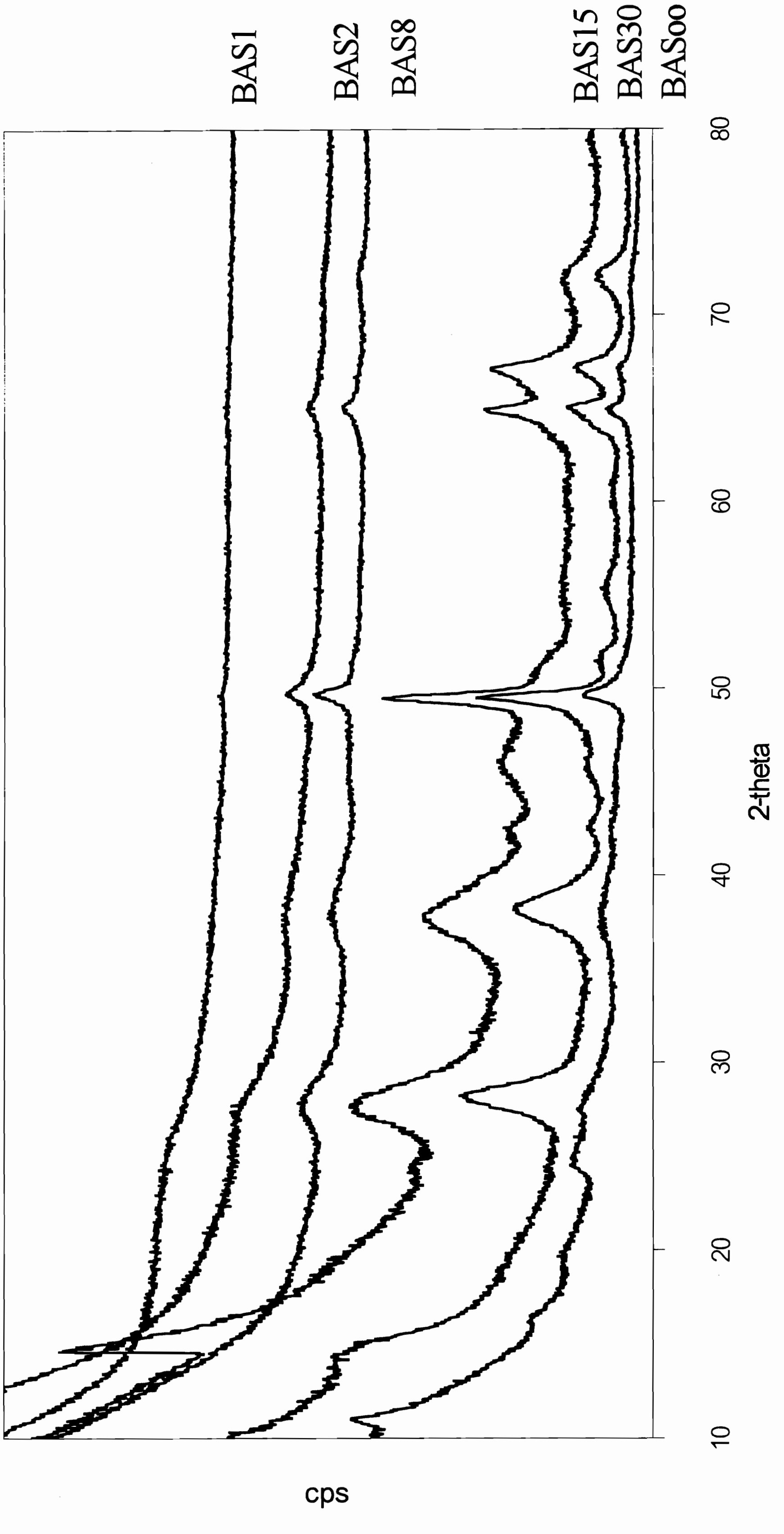

Figure 1b: XRD patterns of precursor gels obtained by the reaction of AIP and TEOS in 1-butanol

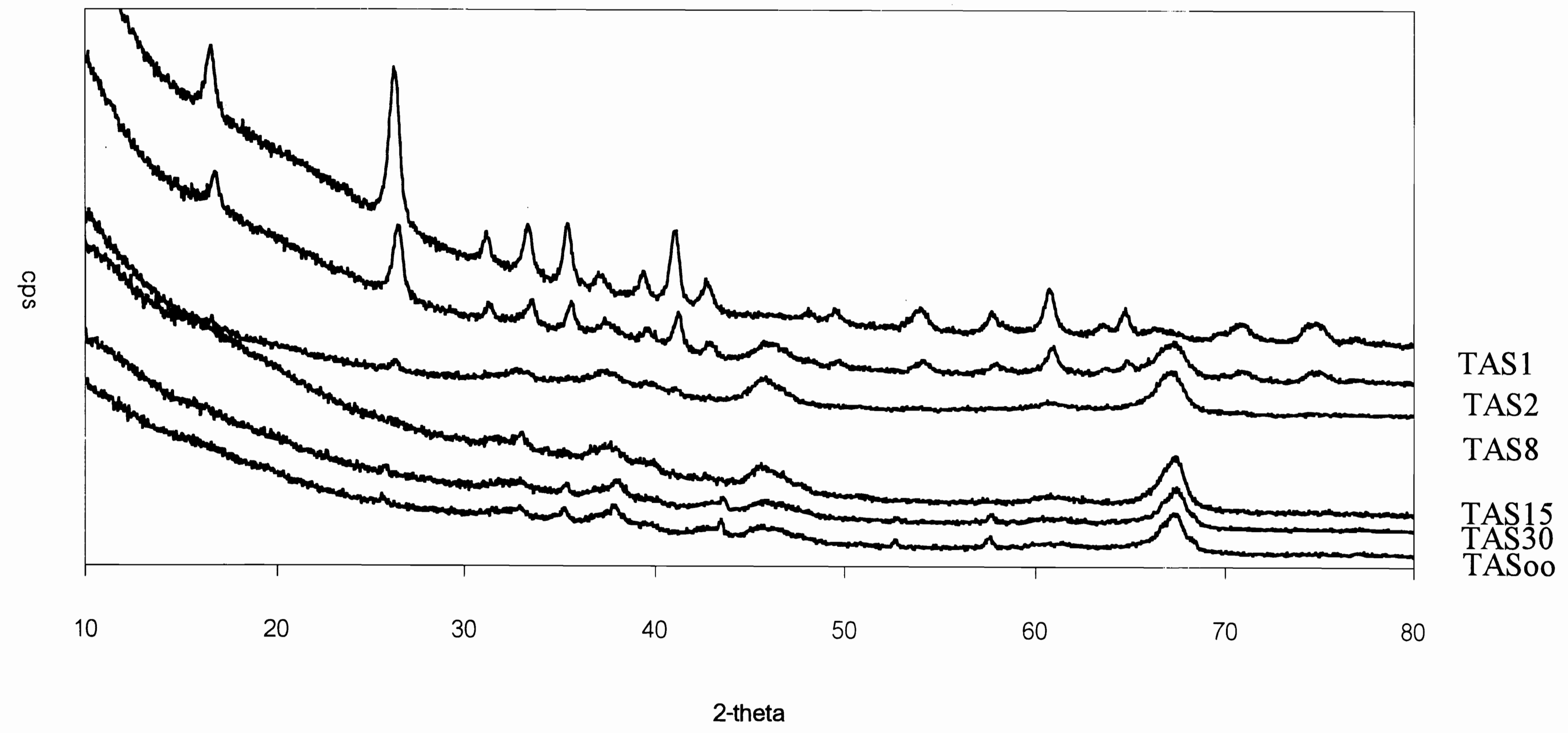

Figure 2a: XRD patterns of the silica-modified alumina precursor obtained by calcination at 1150 °C of the precursor gels prepared in toluene

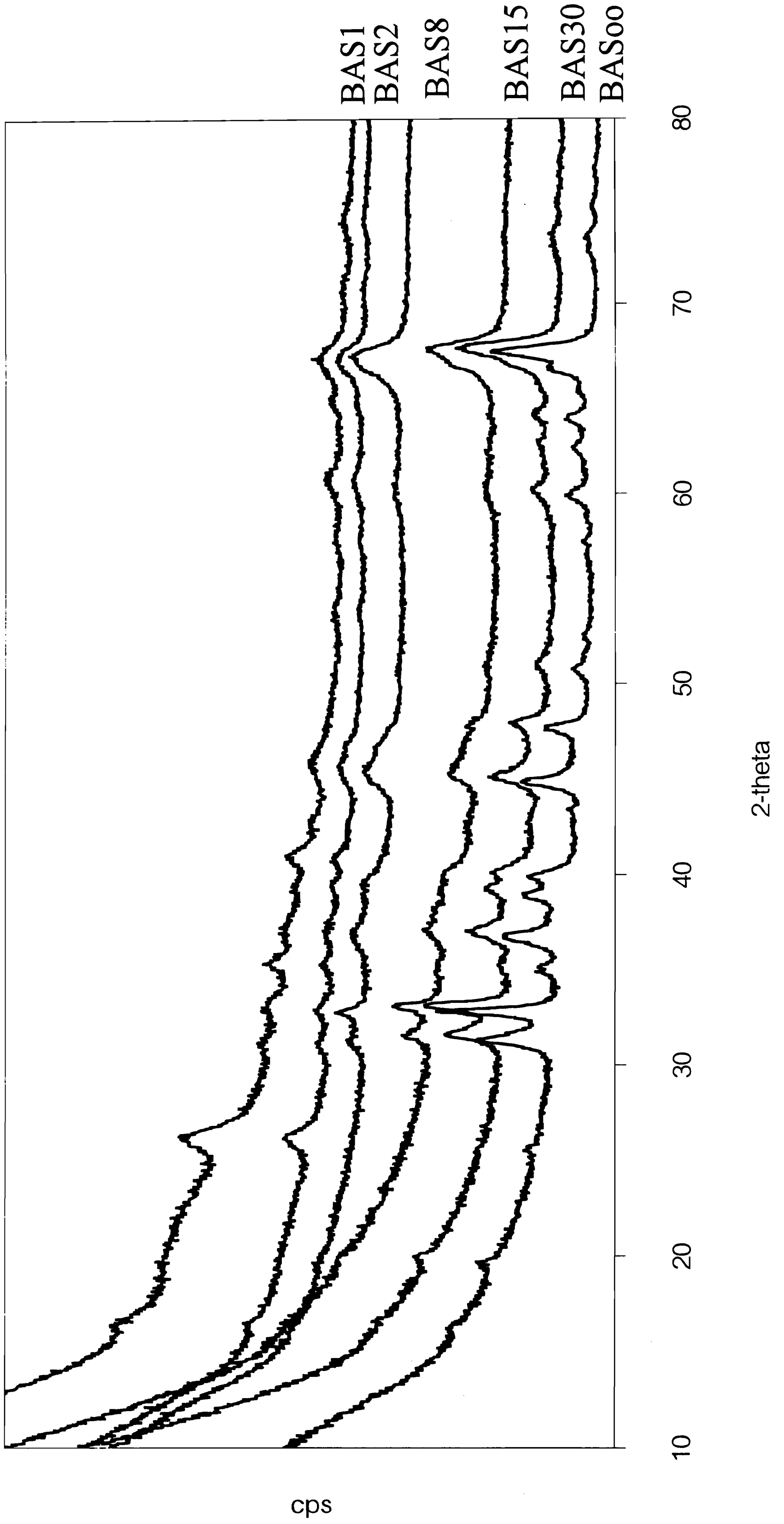

Figure 2b: XRD patterns of the silica-modified alumina precursor obtained by calcination at 1150 °C of the precursor gels prepared in 1-butanol

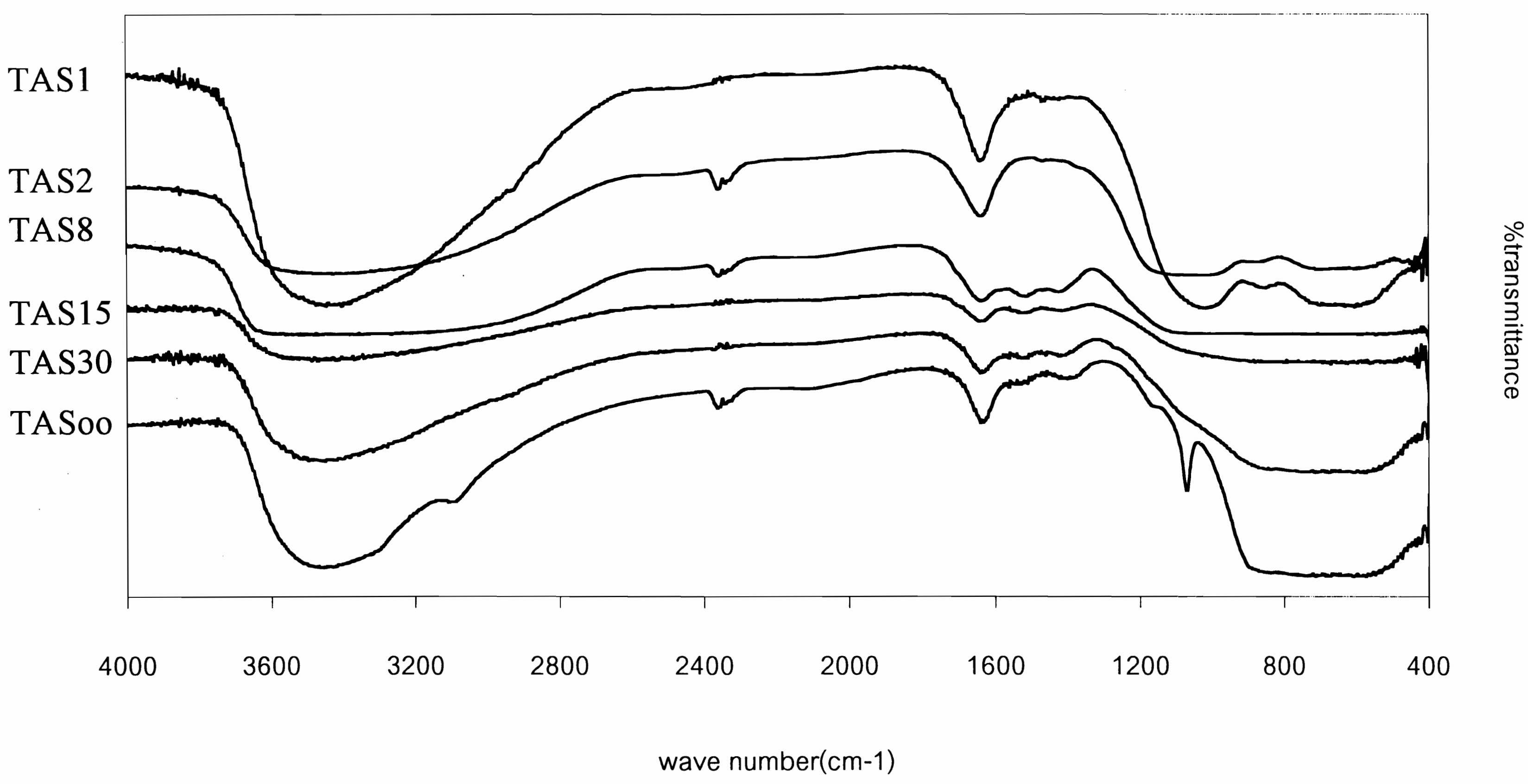

Figure 3a: IR spectra of precursor gels for silica-modified alumina obtained by the reaction of AIP and TEOS in toluene with various TEOS contents

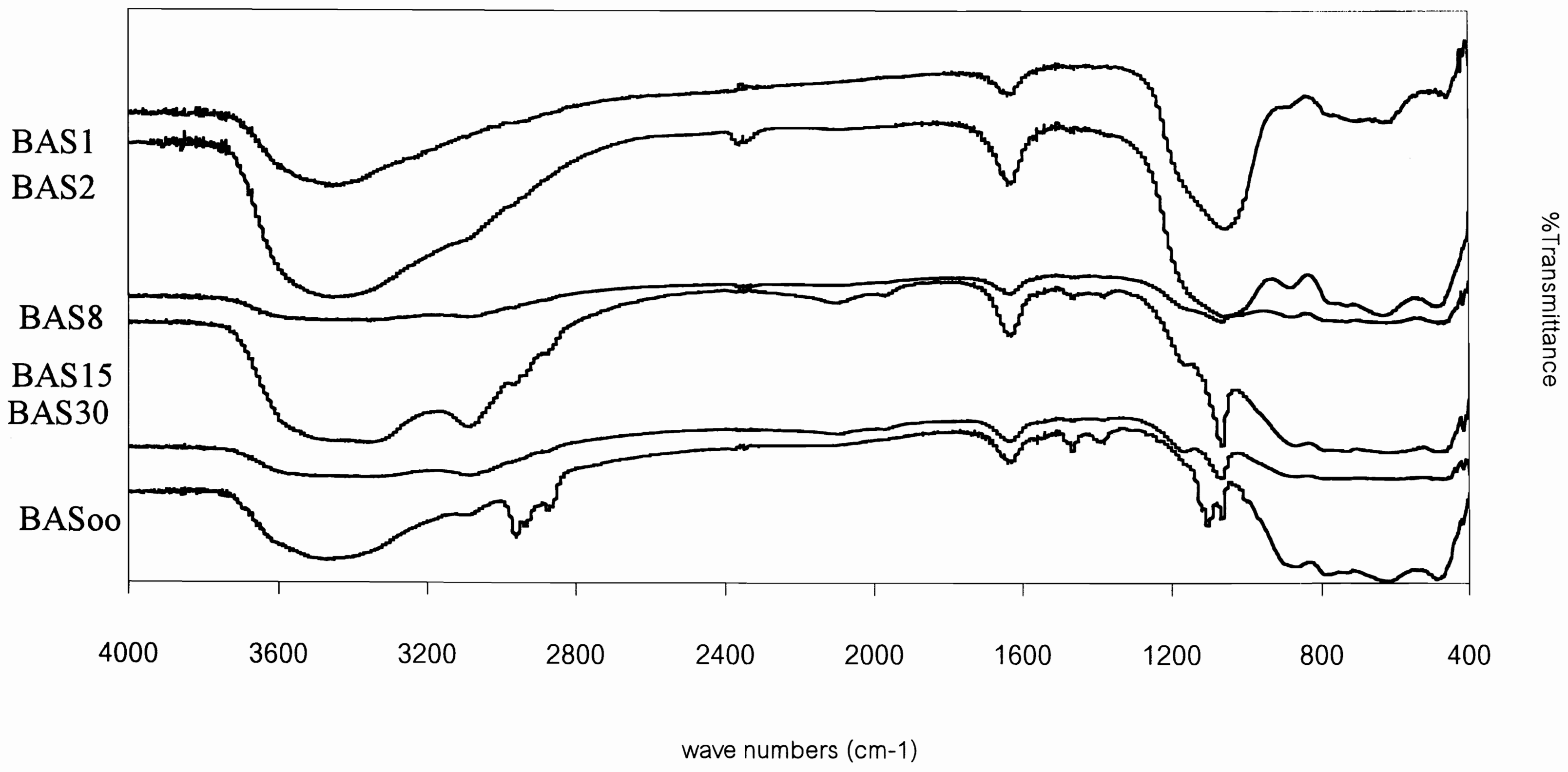

Figure 3b: IR spectra of precursor gels for silica-modified alumina obtained by the reaction of AIP and TEOS in 1-butanol with various TEOS contents

The XRD patterns of BAS1(1150) and BAS2(1150) indicate the presence of mullite and spinel phases, while the XRD patterns of BAS∞ (1150), BAS30(1150) and BAS15(1150) are due to θ-alumina. The XRD pattern of BAS8(1150) can be assigned as the spinel phase.

The effect of the composition of starting materials (AIP/TEOS weight ratio) on the BET surface area of silica-modified alumina after calcination at various temperatures is shown in Figure 4. When products were prepared in 1-butanol, the product with AIP/TEOS weight ratio 8 had the highest surface area at every calcination temperature including 1150°C. In toluene, the product with AIP/TEOS weight ratio 15 had a highest surface area at 1150°C, 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 seems to be due to the crystallization of mullite phase at relatively low temperature.

For the third preparation method, the product with the AIP/TEOS weight ratio 8 was prepared in toluene and a small amount of water was added in the gap between beaker and autoclave wall. The product was colorless powder. When structure of the product was measured by XRD, its XRD pattern was similar to BAS8.

IR spectra of the products are shown in Figure 5. Band characteristics of the boehmite structure were seen at 773, 615, 478 cm^{-1}. These adsorption bands were similar to BAS8.

The XRD patterns of BAS8 and HAS8 are compared in Figure 6. At every calcination temperature, HAS8 showed similar XRD pattern as BAS8.

The BET surface areas of products are summarized in Table 1. It has been found that H1AS8 and H3AS8 had larger surface area than TAS8 at each calcination temperature. The obtained results suggest that the mechanism of reaction in toluene was difference from the other two reactions and comparison of the results between HAS8 and BAS8 shows that these reactions took place by the same reaction mechanism.

Discussion

Reaction in toluene occurred by thermal decomposition of aluminum isopropoxide. Inoue, *et al.* (1993) explained that the direct cleavage of C-O bonds was the prime factor leading to the decomposition of zirconium alkoxide in toluene. Therefore, in the first step aluminum isopropoxide was decomposed yielding Al-O$^-$ and $(CH_3)_2CH^+$ and in the second step nucleophilic attack of Al-O$^-$ on tetraethyl orthosilicate or another AIP molecule took place yielding the Al-O-Si or the Al-O-Al. The lattice finally gave χ-alumina.

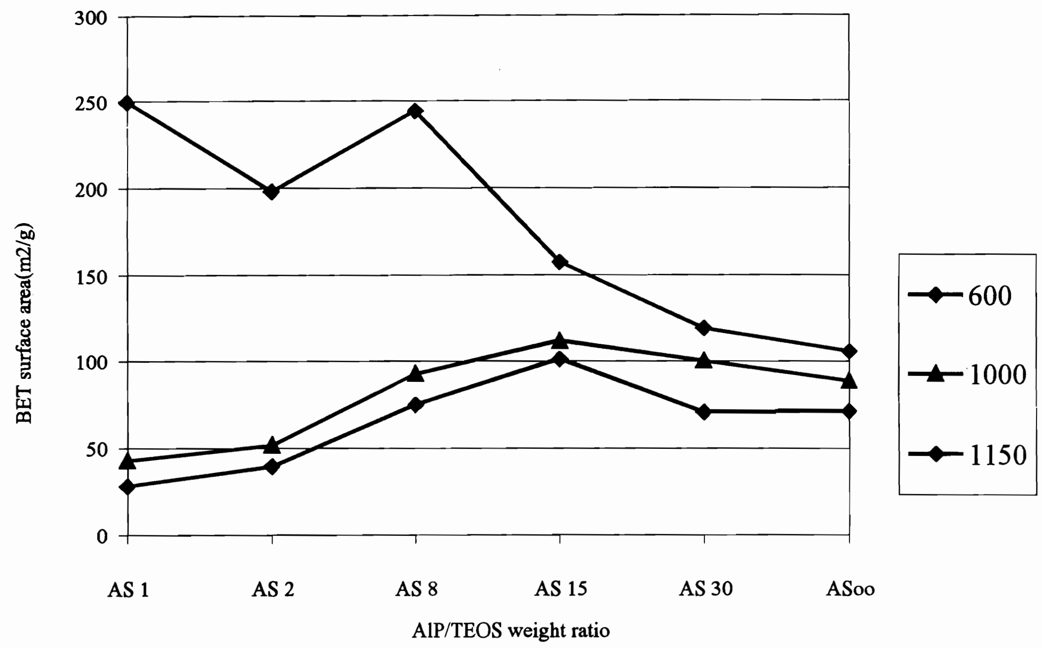

Figure 4a: BET surface area of silica-modified alumina prepared in toluene and calcined various temperatures

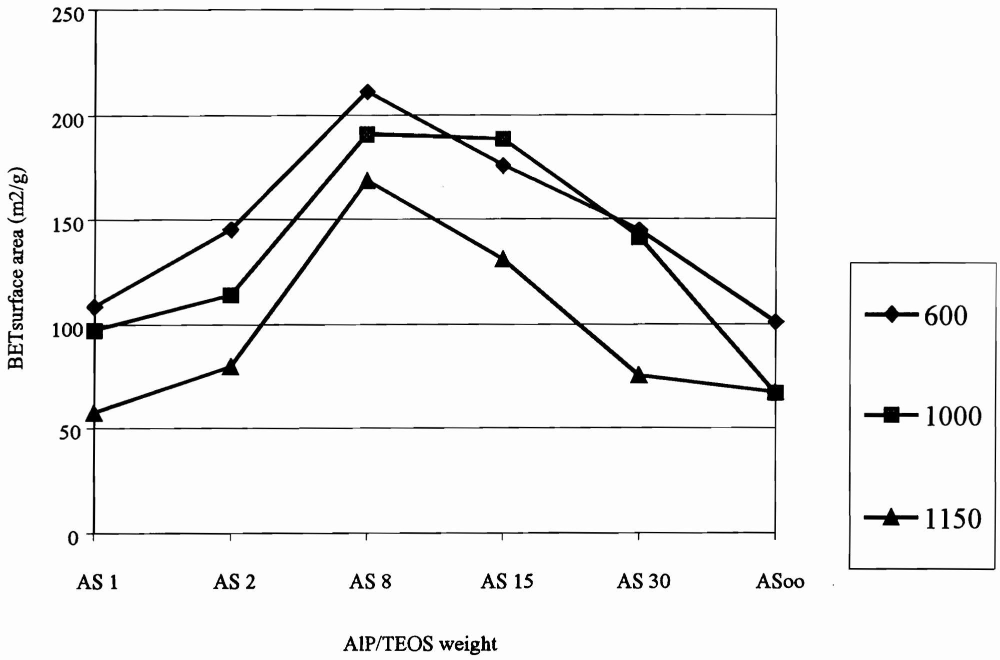

Figure 4b: BET surface area of silica-modified alumina prepared in 1-butanol and calcined various temperatures

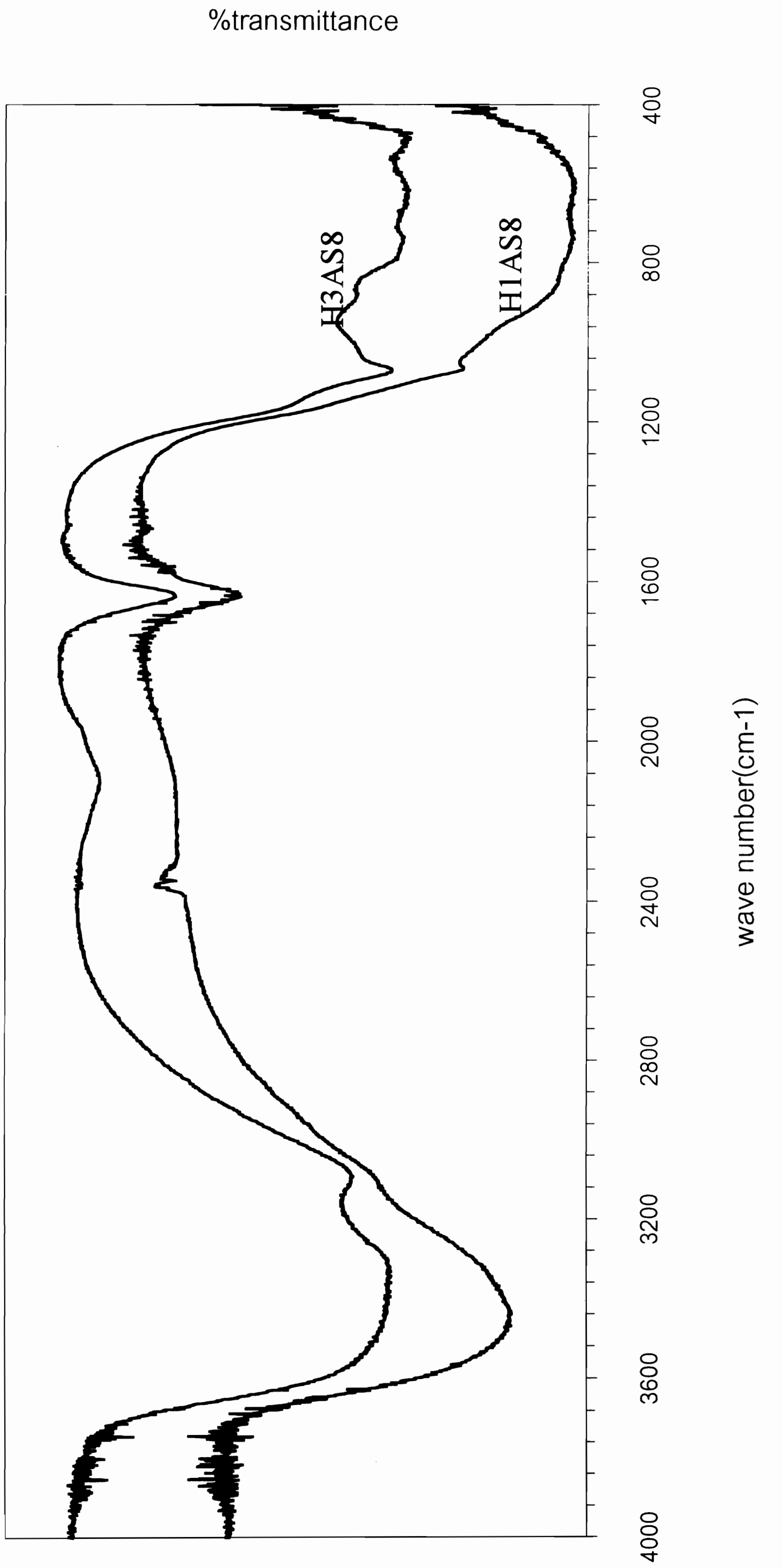

Figure 5: IR spectra of the products obtained in toluene with the addition of water in the gap between the beaker and autoclave wall

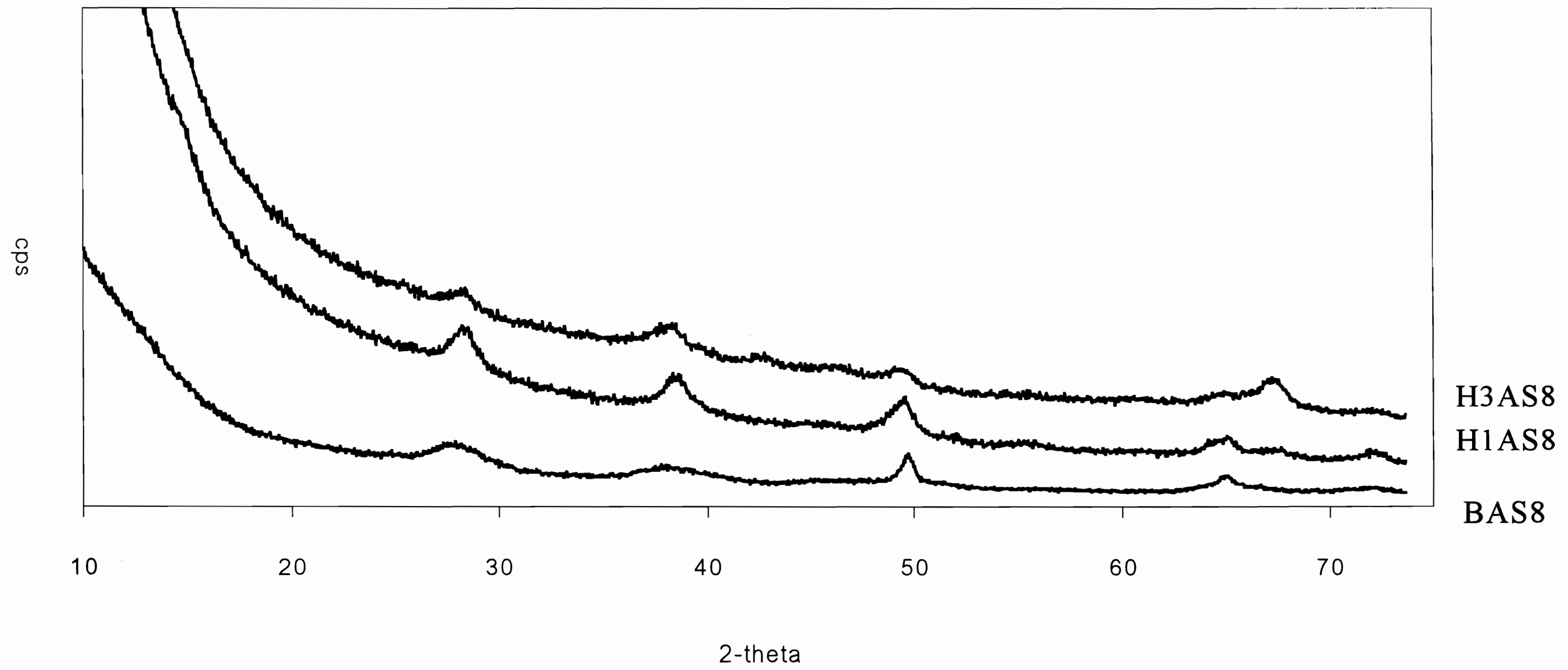

Figure 6a: XRD patterns of precursor gels obtained in 1-butanol and toluene with the addition of water in the gap

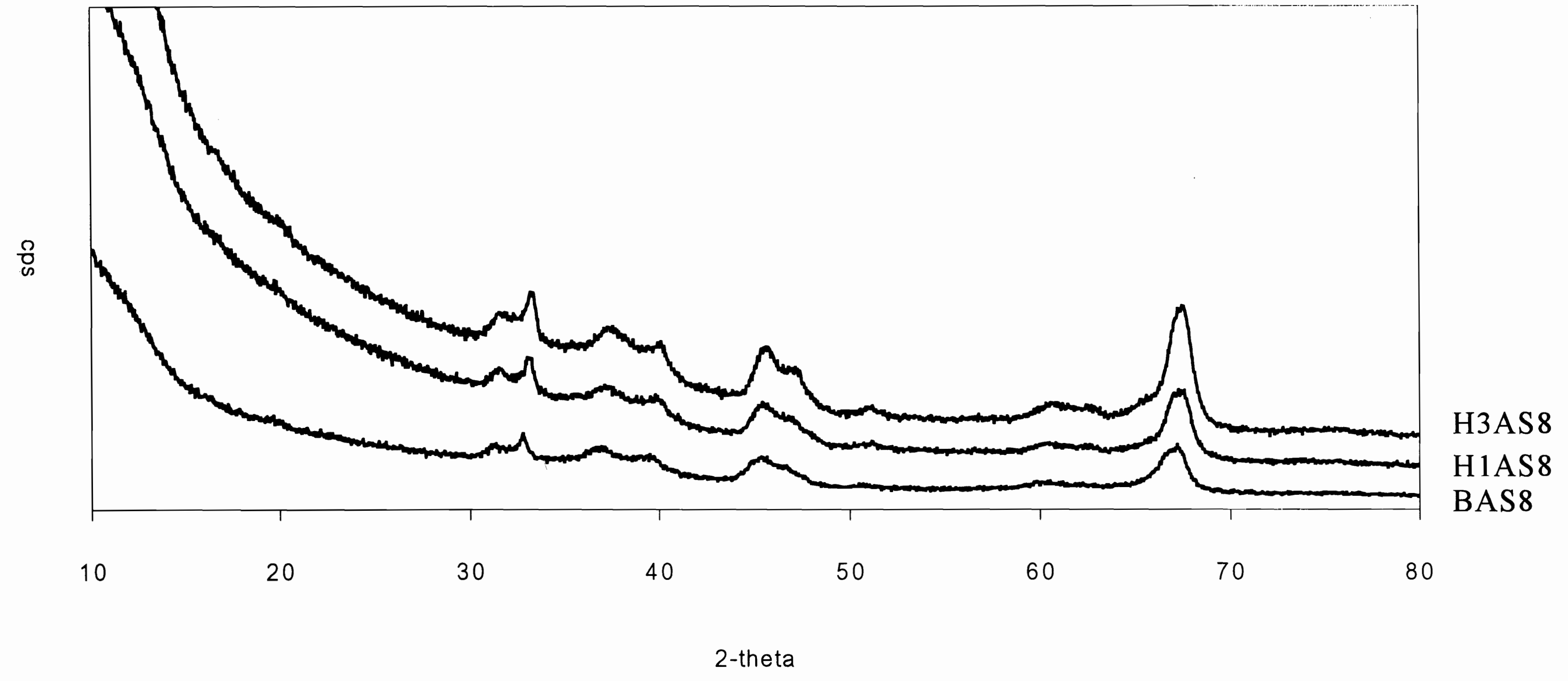

Figure 6b: XRD patterns of precursor gels obtained in 1-butanol and toluene with the addition of water in the gap at calcination temperature of 1150°C

Table 1: BET surface area

AIP/TEOS weight ratio	BET surface areas (m^2/g) at various calcination temperature ($^{\circ}C$)		
	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
TA1	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
BA1	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

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 yielding pseudoboehmite. During the polymerization reaction, the alumina species might react with TEOS remaining the silicon moiety between boehmite layers. For this explanation Kominami, *et al.* (1999) explained the behavior of the water in the gap in the reaction of titanium n-butoxide. However the thermal decomposition of titanium n-butoxide could not occur in toluene but AIP could.

Inoue, *et al.* (2000) found that the treatment of aluminum alkoxide in the alcohol yielding the alkyl derivative on boehmite. When 1-butanol was used as the solvent in the reaction, AIP reacted with 1-butanol yielding 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 more 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 is well known that silica-alumina has strong acidity and therefore the products also has strong acidity. Once small amount of product having Al-O and Si-O bonds are formed, surface acidity of the products dehydrates the solvent, 1-butanol, yielding water, which then hydrolyzes aluminum alkoxide yielding pseudoboehmite. Therefore, addition of small amount of TEOS in the starting mixture completely altered the reaction sequence.

From BET surface areas of the products shown in Table 1, the products obtained in toluene had lower surface area at high calcination temperature than the products obtained in the presence of water in the gap between the autoclave wall and the beaker. This result indicates the effect of water on the reaction. However the surface areas were far lower than that of the product obtained in 1-butanol, the results suggests that the reaction in toluene having water in the gap proceeds by two routes: water dissolved in toluene hydrolyzes AIP, while thermal decomposition of AIP could occur. High thermal stability of product obtained in 1-butanol suggests that the hydrolysis of AIP substantially occurred.

Iler (1964) suggested that silica reacts with alumina to form an extremely vicous 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 that 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 packing of alumina. However, the powders had low surface areas, 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 bonds from hydroxyl. Beguin, *et al.* (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 for 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 seems 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.

The above statement 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 calcined temperature including 1150°C. In toluene, the product having 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, the highest thermal stability of each product was obtained at different AIP/TEOS weight ratios. BAS8 and TAS15 were found to have highest thermal stability. The XRD patterns of TAS8(1000) and TAS8(1150) had peaks 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 stronger 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 show that silicon atoms could readily bond with aluminum atoms in boehmite structure. This was similar to those obtained from the products prepared in 1-butanol, BAS. Therefore, the AIP might also be hydrolyzed with water to form boehmite, leading to the better bonding between Si and Al for the formation of spinel phase.

Conclusion

The reaction of AIP and TEOS in toluene gave products having the χ-alumina structure. When water was added in the gap between the beaker and the autoclave wall, the product had the structure of boehmite. It is the same for the product synthesized in 1-butanol. When temperature rose, water in the gap evaporated and then dissolved in toluene. AIP was hydrolyzed by this water. In 1-butanol when temperature rose, 1-butanol was dehydrated and gave water hydrolyzing AIP. The BET surface area depended on the structure of the product. The products prepared in toluene had the highest surface area at AIP/TEOS weight ratio = 15, but the products prepared in 1-butanol had the highest surface area at AIP/TEOS = 8. Because a limited amount of silicon atoms can be homogeneously incorporated in the aluminum matrix, the results indicated when the products had the boehmite structure, aluminas obtained thereof could incorporate with amount of silica in spinel phase stronger than aluminas obtained from χ-alumina could. BAS8 had the highest thermal stability. It had high surface are of 169 m^2/g even after calcination at 1150°C

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