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Infrared Spectroscopy Studies on Sol-gel Prepared Alumina Powders

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Gamma-alumina fine particles were synthesized by sol-gel process. Aluminum tri-sec-butoxide (ATB), anhydrous ethyl alcohol (EtOH), water (H_2O) and hydrochloric acid (HCl) were used as starting materials. Different samples were synthesized with EtOH/ATB = 60/1, HCl/ATB = 0.08/1 and H_2O/ATB = 1/1 ratios and calcined at different temperatures. Molar ratios of H_2O/ATB (from 1 to 25) and HCl/ATB (from 0.08 to 0.4) were changed for some other samples, during the synthesizing process. The products were characterized by both XRD and FTIR measurements. Studies were carried out on the effect of calcination temperature and change of H_2O/ATB and HCl/ATB ratios on structure and processes involved in phase transformations.

Keywords: sol-gel, γ-alumina, infrared spectroscopy, hydrolysis ratio, acidity ratio.

1. INTRODUCTION

Among metal oxides, alumina is the most common catalyst and catalyst support used in heterogeneous catalysis; because of its low cost, good thermal stability, high specific surface area, surface acidity and its interaction with deposited transition metals [1]. In addition, alumina is also used as the starting material for the preparation of Al_2O_3 based ceramics. A wide variety of these applications are possible because of the fact that alumina exists in a variety of metastable structures; the so-called transition aluminas (such as β, θ, κ, η, γ) as well as its stable α-Al_2O_3 phase. Among these metastable structures, γ-alumina is a key industrial material with numerous applications in refining and petro chemistry [2 – 4]. Bohemite (alumina oxyhydroxide) is the main precursor used to obtain γ-Al_2O_3. The structural elements in bohemite crystals include double chains of AlO_6 octahedral giving double molecules. The double chains consist of AlOOH molecules that are bridged by oxygen atoms. These chains are parallel [5]. Forming layers with parallel chains exhibit arrangements along the axis *b* and shear along the axis *a*, (perpendicular to the general direction of the OH bond) [6]. Therefore, crystallite unit cells of bohemite are rhombohedra with crystallite plans, such as (001), (100) and (010) [4]. By heating the material to a temperature up to 400 °C, it loses its absorbed water and alcohol and becomes porous and affects on physical and chemical properties of material [6]. Further heating up to 700 °C causes transformation to γ-phase. γ-alumina involves plans of (111), (110) and (100) in which (110) is the most important one with maximum area. γ-alumina with this plan is a stable structure which involves 25 % of one-fold unsaturated tetrahedral aluminum atoms and 75 % of two-fold unsaturated aluminum atoms [7]. Since bohemite to γ-alumina phase transition is topotatic [8] therefore, morphology of γ-alumina particles is directly inherited from the equilibrium morphology of bohemite particles in an aqueous solution. Sol-gel process is the best synthesis method because it can control the properties of final particles exactly. This paper deals with the effect of change in molar ratio of the starting material on the properties of alumina fine particles synthesized by sol-gel process. There are limited reports in this regard. Dumeignil et. al [6] have shown that hydrolysis ratio (ratio of hydrolysis water to the alumina precursor), R = [H_2O]/[aluminum alkoxide] is a key in controlling the properties of sol-gel prepared alumina powders. Their results showed that the structural and acidic properties of the alumina powders could be controlled by adjusting the hydrolysis ratio. Seung-Moon Kim et. al [2] reported the effects of acid to aluminum alkoxide and water to aluminum alkoxide molar ratios on the properties of bohemite and γ-Al_2O_3 obtained by sol-gel process. There is a lack of information regarding the effect of water to aluminum alkoxide and acid to alkoxide ratios on type and intensity of the chemical bonds.

2. EXPERIMENTAL

Aluminum tri-sec-butoxide (ATB) (Merck 98 %) was dissolved and refluxed in absolute anhydrous ethyl alcohol (EtOH) (Merck 99.9 %) for 1h. Hydrochloric acid, the hydrolysis catalyst, was added drop-wise into the solution while stirring and refluxing at 75 °C for 3 h. Eventually, the system was cooled down to room temperature, at this point water was added letting the hydrolysis to complete and give a transparent gel. The gel was placed in a glass vessel and aged for several days. After this treatment, the product was dried overnight at 100 °C. The dried solids were calcined in the air from room temperature up to 400 °C at 2 °C/min, and then from room temperature to 700 °C at 4 °C/min, where they remained for 4 h [9]. The molar ratios of the samples prepared for studying the effect of calcination temperature were EtOH/ATB = 60/1, HCl/ATB = 0.08/1 and H_2O/ATB = 1/1 [1]. For other studies, the samples were prepared with change in only one of these molar ratios keeping other rules constant. In order to identify the various phases present, the crystallinity of as-prepared bohmite and calcined γ-Al_2O_3 powders, X-ray

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diffraction (XRD) studies were carried out with a D4 Bruker X-ray diffractometer with Cu K_α as the radiation source and Ni as the filter. Fourier Transform Infrared spectroscopy (FTIR) measurements were carried out using Shimadzu 8400 Spectrophotometer.

3. RESULTS AND DISCUSSION

FTIR analysis has been used as a useful method to study the difference, transformation of aluminium oxy-hydroxide (Bohemite) and also di-aluminium trioxide. The FTIR spectra of bohemite (AlO(OH)) normally show a broad band in the spectral range of (3300 – 3500) cm^{-1} which is assigned to –OH stretching vibration due to hydrogen bonding formation of this group in the aluminium oxy-hydroxide solid [10]. In this region the intensity and the width of the peak, are related to the amount of –OH group, because of the number of H_2O molecules and consequently hydrogen bond generation [11].The peak at 1635 cm^{-1} [12] is assigned to the bending mode of water molecules in the bohemite structure.The above mentioned (3300 – 3500) cm^{-1} and 1635 cm^{-1} peaks appear in gamma phase of alumina too, but with lower intensity and less width for vibrational stretching and very short intensity for bending mode with respect to the bohemite phase.The vibrational mode of Al–O–Al and Al–O for both bohemite and γ-alumina phases are similar with only very slight difference.

3.1. The effect of calcination temperature

It was observed that an increase in calcination temperature causes a phase transformation from bohemite to gamma phase. Fig. 1 shows three FTIR spectra of alumina powders calcined at three different temperatures. With increasing calcination temperature, both width and intensity of the –OH band stretching mode at around (3200 – 3600) cm^{-1} decrease, which is due to decreasing in number of water molecules. This intensity and width temperature dependences can also be observed for the peak at 1620 cm^{-1} which is assigned to –OH bending vibrational mode which in turn verifies the effect of calcination temperature on FTIR spectra of the samples.

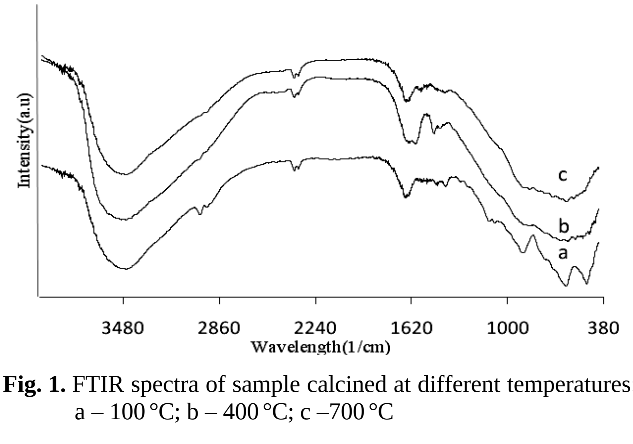

Fig. 1. FTIR spectra of sample calcined at different temperatures: a – 100 °C; b – 400 °C; c –700 °C

Condensation of AlO(OH) into Al–O–Al can also be the other reason for the removal of adsorbed water molecules from bohemite phase and formation of gamma phase under increasing calcination temperature condition. The appearance of moderately weak peaks at 620 cm^{-1} and 485 cm^{-1} for samples calcined at 100 °C and 400 °C are assigned to Al–O stretching mode of AlO_6, respectively. These two small peaks convert into a narrow band for the samples calcined at 700 °C at around 530 cm^{-1}. This observation again emphasizes on converting the phase of the samples from bohemite structure to gamma structure with increasing calcination temperature. This phase conversion was also verified by XRD measurement. With calcination at 700 °C the remained water molecules is removed from samples and a reduction in both –OH stretching and bending modes occurs, which results in complete conversion of bohemite phase into gamma phase.

These observations are in good agreement with the recent report on the disappearing of –OH stretching and bending modes for water molecules after calcination of gibbsite and bohemite [13].

The peak at around 1100 cm^{-1} in Fig. 1 which is attributed to Al–O–C bond, disappears with increasing calcination temperature and finds insignificant intensity at 700 °C [14]. This band disappearing reveals a complete removal of residual organic group from the gel which has been formed from the precursors in sol-gel process [15].

3.2. The change of the molar ratio of water to alkoxide

X-ray diffraction patterns in Fig. 2 show that, both crystallinity and crystallite size of alumina fine particles increase gently from $H_2O/ATB = 1$ to 25 (Fig. 2, a – d) by increasing molar ratio. Not only, more number of crystalline planes, are completed but also width of (440) peak is decreased. Crystalline structure of samples is transformed to complete tetragonal because in addition to (440) plane the other plane such as (400), (311) and (111) have also been appeared [16].

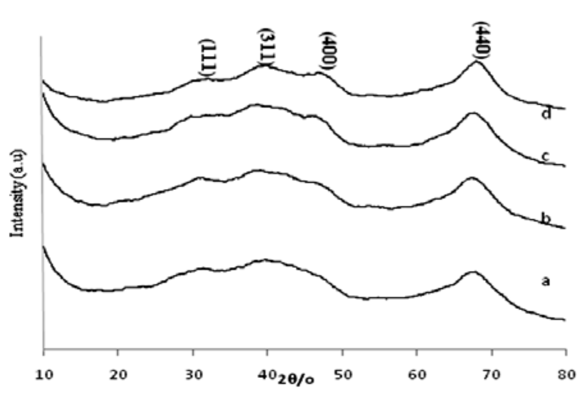

Fig. 2. X-ray diffraction pattern of alumina powders synthesized by sol-gel process and calcined at 700 °C with different H2O/ATB molar ratios: a – 1; b – 2; c – 3; d – 25

In Fig. 3 it is shown that by increasing the H_2O/ATB ratio, the intensity of vibrational modes of water molecule becomes so significant. In sol-gel process two simultaneous reactions, namely hydrolysis and condensation occur when ATB reacts with water. Therefore the amount of water determines the degree of hydrolysis and the type of initial species formed, thus it affects on condensation reaction involved in polymerization of hydrolyzed species in alcoholic medium. By increasing the H_2O/ATB ratio, the ATB gets completely hydrolyzed via following reactions:

$$Al(OR)_3 + 3H_2O \rightarrow Al(OH)_3 + 3ROH; \quad (1)$$

$$Al(OH)_3 \rightarrow AlO(OH) + H_2O; \quad (2)$$

$$Al(OR)_3 + 2H_2O \rightarrow AlO(OH) + 3ROH. \quad (3)$$

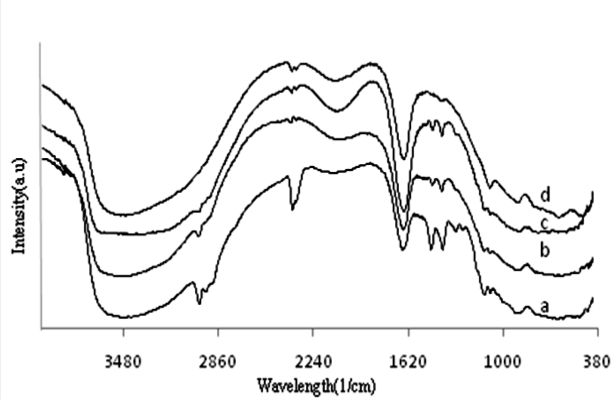

Fig. 3. IR spectra of alumina nanoparticles synthesized by sol-gel process and calcined at 100 °C with H_2O/ATB different molar ratios: a – 1; b – 3; c – 9; d – 25

FTIR measurement was carried out on the as-dried bohemite precursor prepared under different H_2O/ATB ratios to verify the formation of bohemite through reactions (2) and (3). Based on completion of hydrolysis process the absorption band at around (3200 – 3500) cm^{-1} and 1620 cm^{-1}, corresponding to bohemite phase, becomes more broadened and intense. The FTIR spectra shown in Fig. 3 clearly indicate the presence of sec-butoxide group at 1400 cm^{-1} and 1500 cm^{-1} and its $–CH_3$ group at 2950 cm^{-1} related to –OR group which exist on the surface of bohemite. All these bands disappeared based on reactions (2) and (3) by increasing H_2O/ATB ratio for samples H_2O/ATB = 1 to 25 shown in Fig. 3 [2].

3.3. The change of HCl/ATB ratio

In general, acid peptizes the sol and reduces the size of the oligomers to values smaller than the wavelength of the visible light and milky sol transforms to transparent one. In our work, we found that ATB was easily hydrolyzed since non-mother alcohol (Ethanol) was used as a solvent. In addition, the surface of the suspending particles was also charged positively due to pH = 7.4 of the suspension. At this condition, the electrical double layer is destroyed and some particles attract each other by van der Waals forces and large oligomers are generated by formation of transparent gel [17]. The amount of acid affects on rate of hydrolysis so that gelling time reduces with increase of acid amount. Consequently, hydrolysis process proceeds quickly and the rate of condensation increases. No change was found in pH value for the samples prepared by different amount of HCl/ATB ratio in the range of 0.08 to 0.4. Therefore, the added acid has been consumed for pepetization process.

Moreover, this acid can react with hydroxide and facilitates the bayerit to bohemite transformation which results to more number of Al_{13}^{7+} polymeric chains [18].

Al_{13}^{+7} polymers are adsorbed on the particle surfaces and generate short-range inter-particle repulsions which in turn can provide extra forces that leads to decreasing in particles size and consequently causes a phase transformation to γ-alumina [18].

The vibrational modes for Al_{13}^{+7} species appeared at vibrational mode of Al–O bond in AlO_4 [17]. The vibrational bands for (Fig. 4, a and b) and (Fig. 4, c) samples in the region of (400 – 1000) cm^{-1} exhibit the existence of bohemite (Fig. 4). The only sample (Fig. 4, c) experiences a phase transformation, because its vibrational bands have changed in the region (400 – 1000) cm^{-1}, whereas other samples have preserved their own structure and they have only removed physically adsorbed water and alcohol from their own structures. Decrease in intensity of vibrational modes at 1620 cm^{-1} and 3500 cm^{-1} clearly shows this water and alcohol removing.

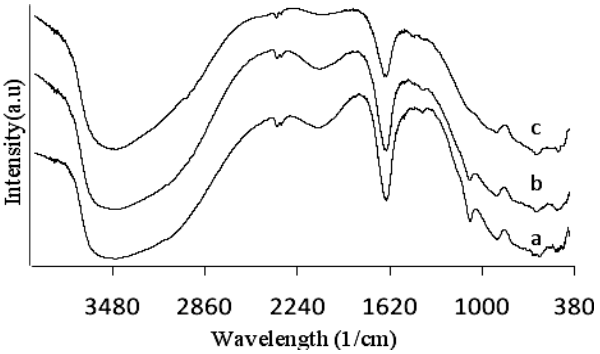

Fig. 4. IR spectra of bohemite particles synthesized by sol-gel process and calcined at 100 °C with HCl/ATB different molar ratios: a – 0.08; b – 0.12; c – 0.40

Formation of loose gel skeleton is the result of fast phase transformation for sample (Fig. 4, c) since phase transformation to γ-phase was supposed to occur at 700 °C. For sample (Fig. 4, b), as soon as Al_{13}^{7+} polymeric chains are produced and adsorbed on particle surfaces, the phase transformation is prevented by acidic of their thermal resistant gel skeleton.

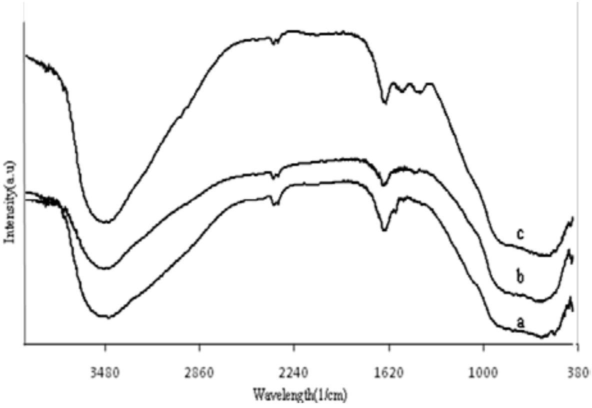

Fig. 5. IR spectra of bohemite particles synthesized by sol-gel process and calcined at 700 °C with HCl/ATB different molar ratios: a – 0.08; b – 0.12; c – 0.4

Fig. 5 shows that all the samples have transformed to γ-phase due to increase in calcination temperature. Vibrational modes in the region of (400 – 1000) cm^{-1} in Fig. 5 show more complete γ-phase structure for sample (Fig. 5, b) since vibrational modes of octahedral and tetrahedral are clearly distinguished for this sample. Although, because of water and alcohol amount among parallel plates of octahedral and tetrahedral Al-O according to high vibrational band approximately at 1620 cm^{-1} and 3500 cm^{-1}, the Fig. 5 for sample (Fig. 5, c) is not acceptable as complete phase transformation of γ-alumina.

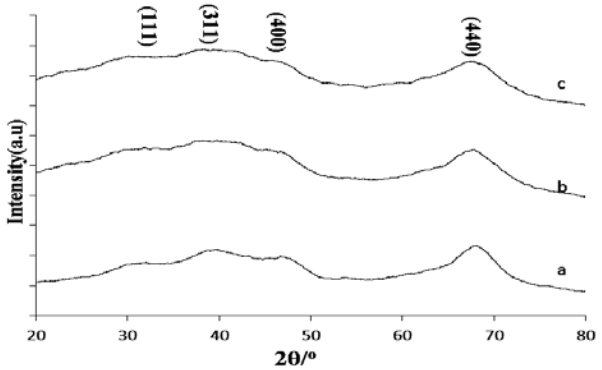

Fig. 6. X-ray diffraction pattern of alumina powders synthesized by sol-gel process abd calcined at 700 °C with different HCl/ATB molar ratios: a – 0.08; b – 0.12; c – 0.4

XRD patterns for the samples prepared by different HCl/ATB ratios are shown in Fig. 6. They show γ-phase for all samples but different crystallinity and crystallite sizes. The most broadening of peak for (440) plane in Fig. 6 shows the lowest crystallite size belongs to sample (Fig. 6, c).

4. CONCLUSION

Alumina fine particles were synthesized by sol-gel process. The phase transformation from bohemite to gamma phase was traced during increase in calcination temperature. FTIR measurement showed that by increasing calcination temperature from 100 °C to 700 °C and removing water molecules from the samples, the intensity and width of the corresponding vibrational and stretching modes were reduced and bohemite structure was converted to gamma structure.

Different samples were prepared with changing in molar ratios of both water and acid to aluminum alkoxide. By increasing H_2O/ATB ratio from 1 to 25, the crystallinity and crystal size of γ-alumina particles were improved. In this case, both hydrolysis and condensation processes were affected which were verified by FTIR analysis.

By increasing HCl/ATB ratio from 0.08 to 0.4, the rate of hydrolysis was increased and gelling time was decreased and extra acid consumed for peptization process rather than changing the pH of the solution. Extra acid facilitated bayerite to bohemite transformation and decreased the size of γ-alumina particles. FTIR analysis revealed that for samples calcined at low temperatures, phase transformation from bohemite to gamma occurred for higher HCl/ATB values and calcination was used for removal of adsorbed water and alcohol molecules. By increasing the calcination temperature, γ-phase was observed for samples with all HCl/ATB ratios.

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