

Synthesis of α - Alumina (Corundum) and its Application

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Abstract

This paper described the preparation of aluminium isopropoxide from aluminium sheet at different heating times. Aluminium sheet is found to have a reaction with absolute isopropyl alcohol and mercury (II) chloride as a catalyst under nitrogen atmosphere. Aluminium isopropoxide was characterized by NMR, XRD and IR. Aluminium isopropoxide serves as a molecular precursor to derive pure alumina gel by hydrolysis under both homogeneous and heterogeneous conditions. Pyrolysis to this alumina gel transforms it into α -alumina (corundum) at 1200°C. The phase transformation during pyrolysis was characterized by XRD, SEM and TEM. The α - alumina (corundum) has porous crystalline nature with high surface area, which may be used as efficient adsorbent packing material in column chromatography for the separation of vitamin A from the leaves. α -alumina can be also used in catalysis.

Keywords : aluminium isopropoxide, alumina gel, α -alumina (corundum), pyrolysis phase transformation, catalysis.

Introduction

In liquid phase chromatography, silica gel (SiO_2 , H_2O), cellulose, or alumina (Al_2O_3) is used as a solid adsorbent. (Moore & Dalrymple 1976), especially alumina (solid adsorbent) is used in the separation of leaf pigments and vitamin A in margarine. The alumina column prevents caking and initiates separation of carotene and other interfering substances.

Aluminas are obtained from the variety of sources. Among them, the hydrolysis of aluminium alkoxide into alumina which has the porous crystalline form and high surface area.

Aluminium alkoxide is one of the metal alkoxides which was developed after world war II. Today the alkoxides of alkali metals, magnesium, titanium, zirconium, antimony and aluminium alkoxides are commercially important. (Kark & Othmer 1982).

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Particularly the aluminium alkoxides of C3 and C-4 alcohols, such as aluminium isopropoxide and aluminium sec-butoxide are of technical importance. In aluminium alkoxide, superficially there appear to be three (OR) groups around the central Al, but in fact the alkoxides are polymeric, eg, aluminium isopropoxide is trimeric, but slowly rearranges to the tetramer on standing (Davison. 1961).

Aluminium alkoxides are easily soluble in aromatic and chlorinated hydrocarbons, but sparingly soluble in alcohols. It is sensitive to moisture and therefore dry storage is essential.

Aluminium alkoxides are used extensively as molecular precursors such as mesoporous oxides from thermal treatment of aluminium alkoxides (Yang. 1998), alumina gel from hydrolysis of aluminium alkoxides (Stumpf, *et al.* 1950) and the alumina and silica sols from aluminium isopropoxide with tetraethylorthosilicate (Gulnihal. 2002).

The present paper involves the studies on aluminium isopropoxide from aluminium sheet and purified by isopropyl alcohol, alumina gel from the sol-gel hydrolysis of aluminium isopropoxide, activated alumina from pyrolysis of alumina gel at different heating times. This activated alumina gel can be used in chromatography, dehydrating agents, ion exchange materials and catalysts.

Alumina occurs in a variety of forms. It is common constituent of many rocks and minerals but it is also found in the free state as the oxide or hydroxide. Aluminium oxide occurs in nature as corundum which has the crystalline type. Aluminium hydroxide may be prepared in amorphous or crystalline forms. Freshly precipitated aluminium hydroxide is amorphous but aging gives crystals (Searle. 1959).

The hydrolysis of aluminium isopropoxide gives alumina xerogel (porous). Amorphous alumina xerogel was prepared in an aqueous medium and amorphous alumina aerogel was prepared in a non-aqueous medium. Foster and Keys showed that the best aerogels and xerogels have about the same activity (Kerker. 1977).

Several crystalline hydrates exist namely the α and β -trihydrate (gibbsite and bayerite) and the α and β monohydrate (boehmite and diaspore) and anhydrous alumina namely α -alumina (corundum) (Day & Hill 1953).

Thermal decomposition of the various alumina hydrates yield a number of crystalline variations of alumina which are transition stages in a process eventually yielding anhydrous alumina corundum. Alumina the amorphous crystallines to the α - crystalline modification at a temperature between 500-1000°C and at higher temperatures it is converted to the α -form, known as corundum (Searle & Grimshaw. 1959).

Corundum is stable above 450±5°C. Diaspore is stable 280 to 450±5°C and boehmite apparently is stable between 155°C and 280°C. Gibbsite is unstable above 155°C. Bayerite is unstable above 155°C, while the indications are that it is less stable than gibbsite below this temperature (Laubengayer & Weisz. 1943).

During drying, some of the crystalline phases such as the α - and β trihydrate and α -monohydrate have been examined by X-ray diffraction analysis. The dried alumina gel can be activated by heating and is porous with high surface area, which makes it useful as an adsorbent (Harris., *et al.* 1958).

Experimental

The chemical suppliers were from British Drug House (BDH) Chemical Co., Ltd., England Kanto Chemical Co., Ltd., Japan and Fisons Scientific Equipment, Loughbrough, England. These chemicals were used as it was received unless otherwise stated.

The apparatus used included a balance (E. Mettler, Switzerland), a magnetic heating and stirring (Volts - 230, Hz ~ 50, UK by Bibby Sterilini Ltd.), X-ray diffraction (XRD Rigaku D-Max 2200, Japan), a muffle furnace (Model L - 3333, Australia), a vacuum oven (Gallenkamp) Edward EB 3A vacuum pump and compressor, England and a glass ware (Pyrexglass).

The experimental work was carried out in two categories. The first involve the preparation of aluminium isopropoxide by the reaction of aluminium sheet, purified isopropyl alcohol and mercury II chloride used as catalyst under nitrogen atmosphere. The solution mixture was placed in a round-bottomed flask, provided with an efficient reflux condenser. The flask is gently warmed in a stream-bath and gentle refluxing maintained at different heating times. The product was purified

by distillation under vacuum. This fine product was characterized by melting point, NMR, XRD and IR.

The second included the preparation of the alumina gel by hydrolysing aluminium isopropoxide under homogeneous and heterogeneous conditions. Under homogeneous condition, the solution of aluminium isopropoxide in absolute isopropyl alcohol with an equal volume of a solution of water in isopropyl alcohol were stirred for about 3 hrs. The gel was formed by centrifuging and was washed once with isopropyl alcohol. The sample was dried by vacuum oven.

Under heterogeneous condition, the solution of aluminium isopropoxide in benzene with an equal volume of water were stirred for about 15 mins. The gel was formed and then it was mixed with isopropyl alcohol. After the separation of the mixture, the gel was washed with water three times and washed once with isopropyl alcohol.

Then the alumina gels from two methods were heated in a furnace at selected temperatures (ambient temperature, 200°C, 400°C, 800°C and 1200°C) to obtain activated alumina. For each temperature the alumina gel was kept for 1-hr. The phase transformation of this alumina gel was then characterized by XRD, SEM and TEM.

Results and Discussion

In the synthesis of aluminium isopropoxide, excess amount of purified isopropyl alcohol and aluminium such as aluminium sheet, aluminium powder with mercury II chloride as catalyst were used at different heating times. Among them, the synthesis using aluminium sheet is efficient. The yield % of aluminium isopropoxide prepared from aluminium sheet at different heating times were shown in Table 1.

Table 1. Effect of reaction time on the aluminium isopropoxide prepared using aluminium sheet ($95 \pm 5^\circ\text{C}$)

No	Time	Yield (%)
1	1	-
2	3	15.00
3	5	87.00
4	7	88.13
5	9	88.25

The heating times were different about ± 2 hrs from one another. Increasing the heating time, the yield % also increases. But when the heating time is above 5 hrs the yield % becomes close to one another. On the basis of these results. 7 hrs of heating time is suitable for the optimum time.

Aluminium isopropoxide was characterized by NMR spectroscopy. Aluminium isopropoxide in CDCl_3 was recorded at 300 MHz NMR spectrophotometer and the spectrum is shown in Figure 1. It consists of three doublets and two septets. The high field doublet representing 36 equivalent protons reveals 12 terminal methyl groups which absorb at δ 1.13 ppm (with $J = 6$ Hz).

The two doublets absorb at lower field are two sets of non-equivalent methyl protons of bridge isopropyl groups, each set containing 6 methyl groups appear at δ 1.29 ppm and 1.48 ppm (with $J = 6$ Hz).

Two septets at δ 4.53 ppm and 4.23 ppm represent two non-equivalent methine protons of isopropoxy groups. On the basis of the NMR spectrum, this compound can be tetrameric aluminium isopropoxide. The chemical shift value and interpretation of aluminium isopropoxide is reported in Table - 2.

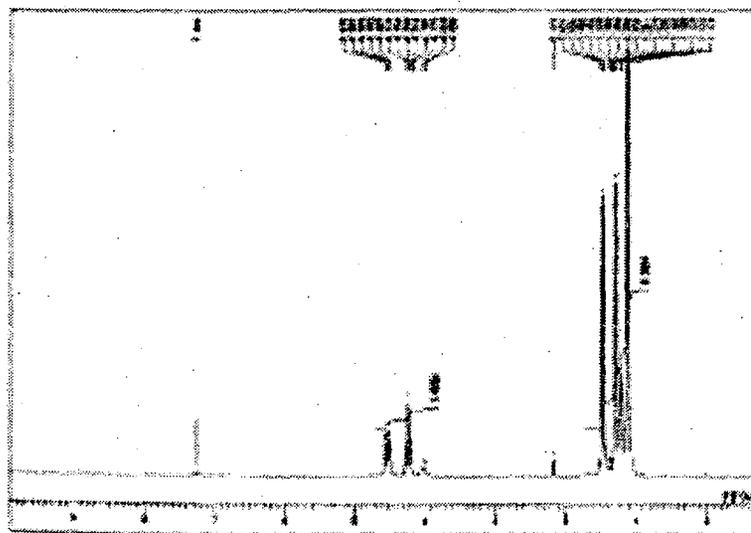


Figure 1. ^1H NMR spectrum of aluminium isopropoxide

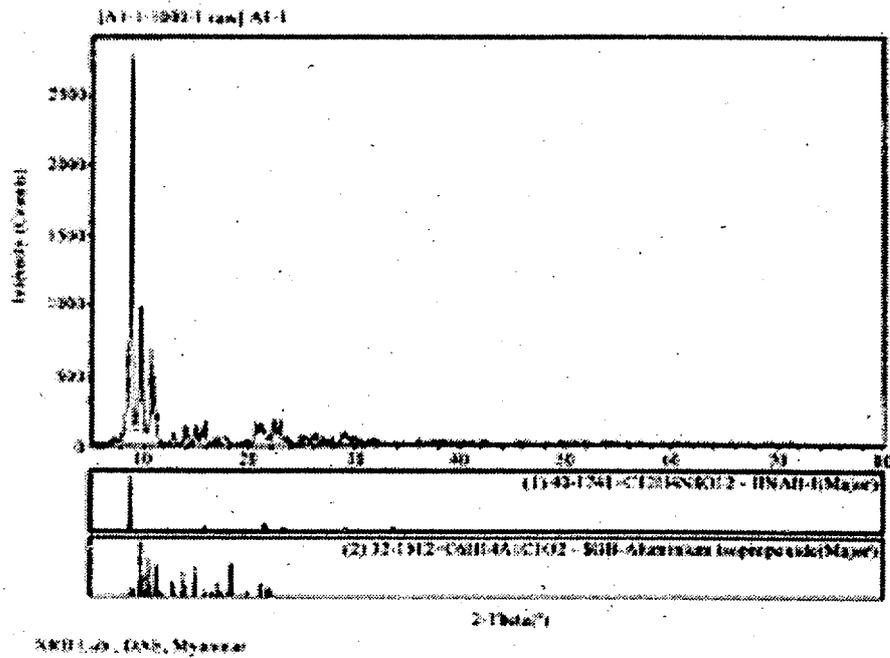


Figure 2. XRD spectrum of aluminium isopropoxide

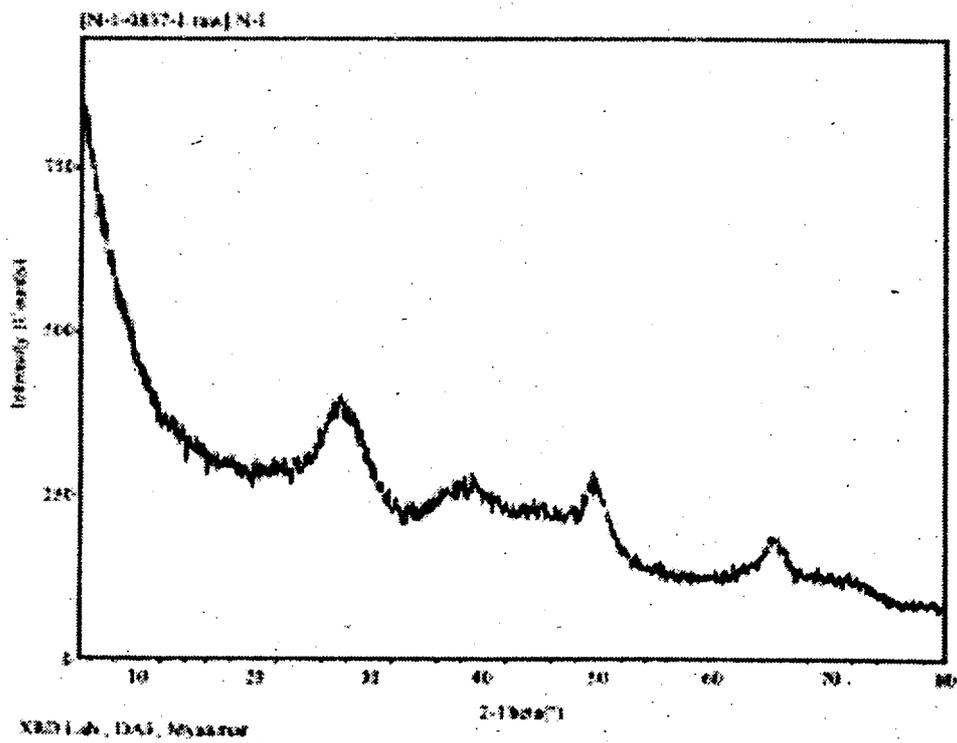
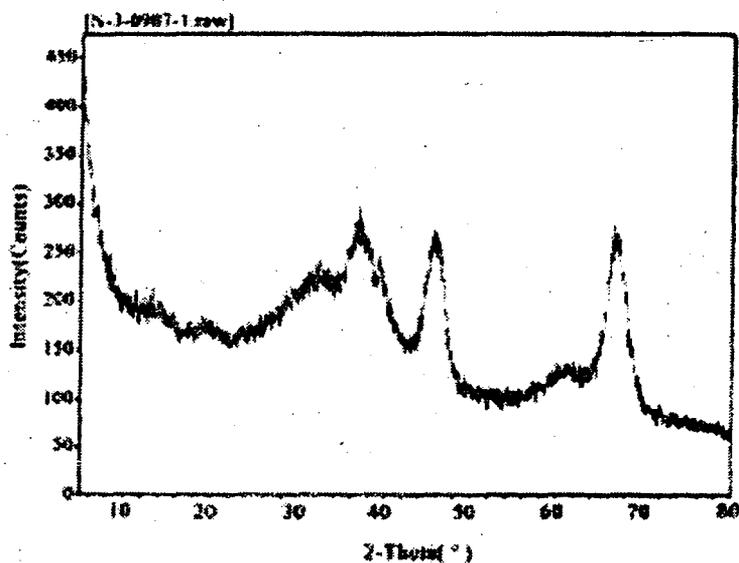
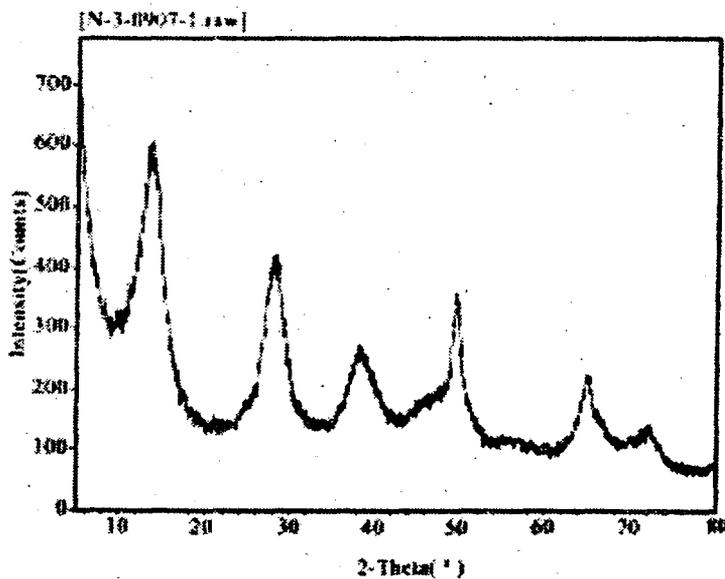


Figure 3 (a). XRD spectrum of alumina gel at ambient temperature



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Figure 3 (b) . XRD spectrum of alumina gel at 200°C



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Figure 3 (c) . XRD spectrum of alumina gel at 400°C

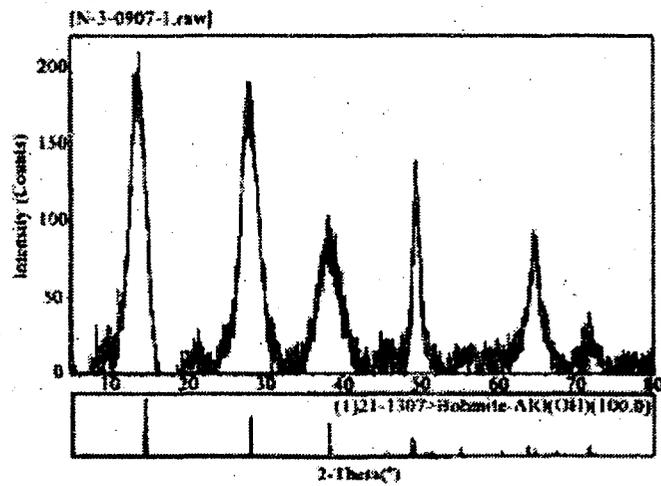


Figure 3 (d) . XRD spectrum of alumina gel at 800°C

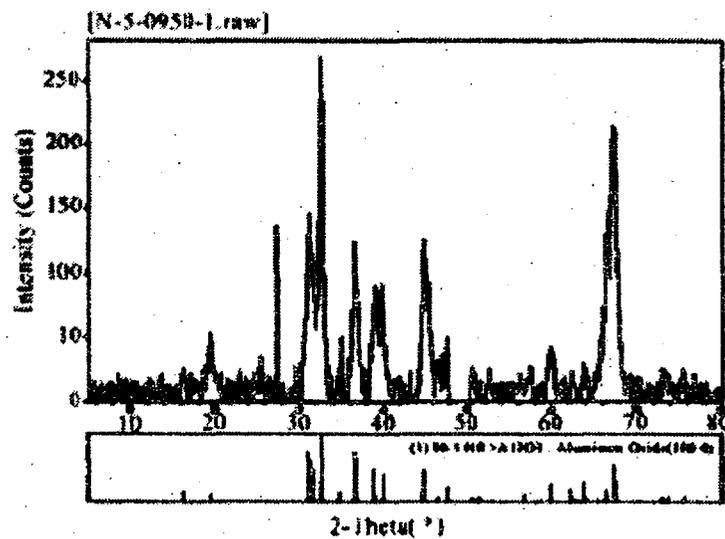


Figure 3 (e) . XRD spectrum of alumina gel at 1200°C (homogeneous condition)

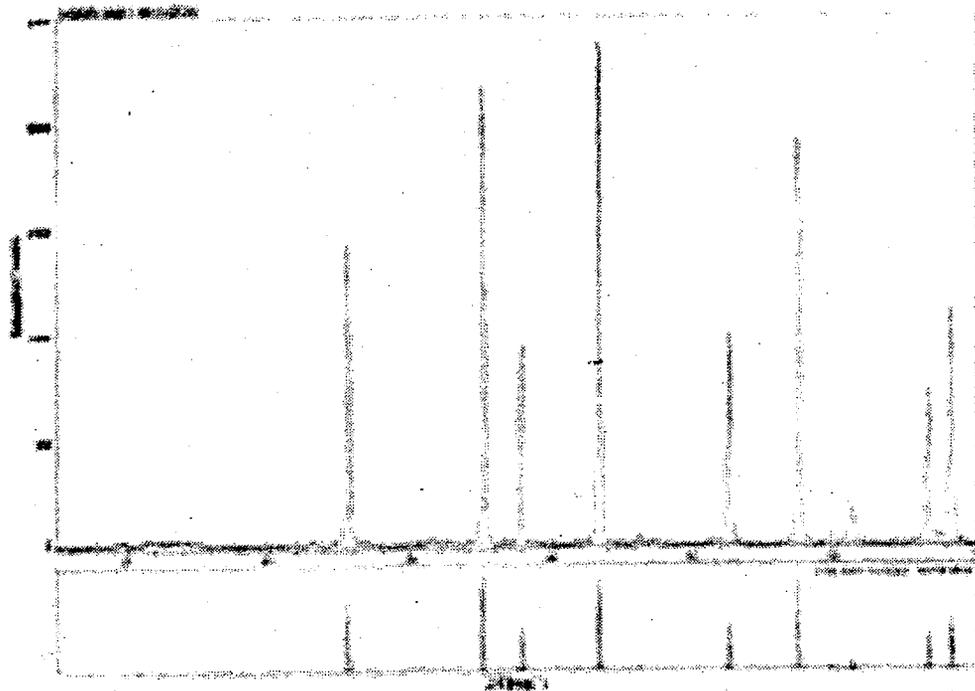


Figure 3 (f) . XRD spectrum of alumina gel at 1200°C (heterogeneous condition)

Table 2 . NMR spectrum assignment for aluminium isopropoxide

δ (ppm)	Multiplicity	Integration	Assignment
1.48	doublet (J= 6 Hz)	6 H	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2- \end{array}$
1.29	doublet (J= 6 Hz)	6 H	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2- \end{array}$
1.13	doublet (J= 6 Hz)	6 H	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2- \end{array}$
4.53	septet (J= 6 Hz)	1 H	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}- \end{array}$
4.28	septet (J= 6 Hz)	1 H	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}- \end{array}$

X-ray diffractogram also indicates the crystalline nature of aluminium isopropoxide as shown in figure 2.

The alumina gel was prepared by hydrolysing aluminium isopropoxide under homogeneous and heterogeneous conditions at ambient temperature. The X-ray diffractogram of this alumina gel from two methods are similar pattern in Figure 3 (a) which indicates the amorphous nature. This alumina gel was pyrolysed at selected temperature (200°, 400°, 800° and 1200°C). During pyrolysis, the weight loss % of alumina gel is shown in Table - 3.

Table 3 . The weight loss % of alumina gel at certain various temperature.

No	Temperature (°C)	Mass (g) (before pyrolysis)	Mass (g) (after pyrolysis)	Weight Loss(%)	%Difference theoretical
1	200	0.5	0.4295	14.1	4.19*
2	400	0.5	0.3781	24.38	4.66
3	800	0.5	0.3297	34.06	4.38
4	1200	0.5	0.2787	44.26	4.91

Increasing the pyrolysis temperature, the weight loss % were increased. This means that at lower temperature, the water molecule was left in the alumina gel. At 1200°C, all the water molecules were released from the alumina gel, which indicates the crystalline nature.

X-ray diffractograms can also be used to identify these results. After pyrolysis at selected temperatures such as 200°C, 400°C and 800° C, the XRD patterns of alumina gels from two methods are similar patterns in Figure 3-b, 3-c and 3-d. At these temperatures, the XRD patterns exhibit broad maxima, characteristic of amorphous material.

At 1200°C the different XRD patterns of alumina gels from two methods are shown in Figure 3-e and 3-f. Figure 3-e is shown the crystallization of aluminium oxide (but not corundum) which was obtained from homogeneous condition.

The nature of α -alumina (corundum) which takes place is evidenced by sharp peak as shown in Figure 3.f. XRD data for synthetic α -alumina and standard alumina are shown in Table 4.

Table 4 : X-Ray diffraction data for synthetic α - alumina and standard alumina.

α - Alumina (Standard)			α - Alumina (Synthetic)		
I(%)	d(A)	2-Theta	I(%)	d(A)	2-Theta
100	2.0834	43.394	100	2.0823	43.420
92.0	2.5488	35.181	92.0	2.5461	35.220
80.1	1.6001	57.555	80.1	1.5999	57.560

Conclusion

In this paper, the preparation of aluminium isopropoxide from aluminium sheet was made, and NMR, XRD analysis were carried out. And then α -alumina was prepared by pyrolysing the alumina gel from the hydrolysis of aluminium isopropoxide under homogenous and heterogeneous conditions.

The phase transformation of alumina gel was assessed during pyrolysing. Alumina is used as a solid adsorbent in chromatography to separate chlorophyll and β - carotene from the leaf pigments.

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