

Influence of calcination temperature of prepared Aluminum hydroxide on the activity of active gamma Alumina oxide on the dehydration of ethanol

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Abstract

The active gamma alumina oxide catalyst was prepared by using the precipitation of mixing of aluminum nitrate and aqueous ammonia. The effect of calcinations temperature of aluminum hydroxide on the crystallography of the alumina oxide products were studied by means the thermal analysis and the X-Ray diffraction technique. The calcinations temperature were (300, 500, 600, 650, 700, 800, 900, and 1000) °C. Also the surface area, pore volume, and mean pore radius were measured for all alumina oxide products. The activity of these alumina oxides for dehydration of ethanol was studied and comparable to that of commercial alumina oxide. The reaction was carried out in a tubular reactor under atmospheric pressure and 350°C. While the reaction products were analyzed by gas chromatography technique. The results show that the calcination temperature of 600-650°C gives the active crystal phase of gamma alumina oxide which is exhibit comparable dehydration activity to the commercial catalyst.

Key word: calcinations, Aluminum hydroxide, gamma Alumina, ethanol dehydration

الخلاصة

تم في هذا البحث تحضير الكاما اوكسيد الالمنيوم الفعال بواسطة الترسيب لخليط نترات الالمنيوم والامونيا حيث تم دراسة تأثير درجة حرارة كلسنة هيدروكسيد الالمنيوم المترسب على تغير الاطوار البلورية لاوكسيدالالمنيوم الناتج باستخدام تقنية التحليل الحراري وحيود الاشعة السينية. وكانت درجة حرارة الكلسنة المستعملة

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المساحة السطحية وحجم المسامات ومعدل قطر المسامات لجميع العوامل المساعدة من اوكسيد الالمنيوم المحضر. اما فعالية العوامل المساعدة المحضرة ومقارنتها مع التجارية فقد تم اختبارها في عملية سحب جزئية ماء (dehydration) لليثاقول في مفاعل انبوبي تحت الضغط الجوي ودرجة حرارة $350^{\circ}C$ ثم تحليل نواتج التفاعل باستخدام الغاز كروموتوغرافي. من خلال النتائج التي تم الحصول عليها تبين افضل درجة حرارة كلسنة كانت (600-650) درجة مئوية والتي تعطي الطور البلوري الفعال من الكاما اوكسيد الالمنيوم ذو الفعالية المناسبة والمقاربة لاوكسيد الالمنيوم التجاري كما اكدته نتائج البحث.

Introduction:

The basic properties of the catalyst components are, the main determinant, but texture and stability can be influenced strongly by choosing appropriate method for preparation⁽¹⁾. Active gamma alumina oxide ($\gamma-Al_2O_3$) is extensively used as catalysts, co-catalysts, catalyst-supports and adsorbents⁽²⁾. This is a linear polymer with sidechains, formed by dehydrated aluminum hydroxide groups⁽³⁾. Because of its favorable surface characteristics, almost all of the commercial hydro treating catalyst use $\gamma-Al_2O_3$ as a support^(4,5).

One of the most important means of controlling texture and strength of a catalyst involves the preparation of the catalyst

available. Alumina oxide being widely used because it is inexpensive, reasonably stable and can provide, through its different phases, a wide range of important properties which are suitable for many catalytic applications. The preparative techniques for the precursors and the temperature at which they are calcined have a great influence on the surface area and pore structure which control the activity and selectivity of alumina oxide^(6,7). In the prepare of the active alumina oxide, it is essential to maintain the optimum conditions of aluminum hydroxide precipitation, washing, filtration, drying and especially of calcining. Precipitation is based on hydrolysis of the aluminates anion to alumina hydrate which is a slow process. The size of

crystals and alumina hydrate are controlled by a range of variables including liquor concentration, temperature, holding time, and precipitation rate. the retention time in the precipitators varies between 20-40 hr as shown by McAuley⁽⁶⁾. The drying and calcinations conditions are of critical importance in determining the physical as well as catalytic properties of the product⁽⁹⁾. The objectives of calcinations are a well determined structure of the catalyst, the parallel adjustment of the texture with respect to surface area and pore volume and a good mechanical resistance⁽¹⁰⁾. The exact calcinations temperatures depends on the type of alumina product required and the nature of calciner⁽⁹⁾.

Alumina exists in a number of crystalline form. Only one of these forms-phase is thermodynamically stable. When alumina hydrates are heated dehydration occurs and is accompanied by structural changes. A series of Meta stable intermediates are progressively formed where the stable α -Al₂O₃ being the final product of thermal decomposition⁽¹¹⁾. The transition alumina's that are formed depend on the starting material, the rate

and duration of heating, particle size, atmosphere (air, steam, vacuum) and presence of impurities. α -alumina oxide is the most dense and non-reactive alumina. Three main reactions occur on calcinations of alumina hydrate to α -Al₂O₃. Conversion of tri-hydrate to monohydrate occurs below 250°C as in the following reaction:



The monohydrate is converted to a various crystalline transition states eta, gamma, delta, theta.....etc from a bout 300 – 900 °C



These are then converted to α -Al₂O₃ at a bout 1100°C⁽¹²⁾. Calcinations of alumina hydrate also produce changes in surface area, particle size, pore distribution, stability as well as catalytic activity. Further more calcinations increases the strength of the final catalyst particle by causing crystal phase on compound formation through thermal diffusion, solid state reactions and sintering⁽¹³⁾.

In this paper, the active alumina oxide was prepared by the precipitation method and the effect of calcinations temperature on the characteristics of the catalyst was studied. The dehydration of ethanol was studied as a model reaction to test the catalytic activity of this prepared alumina

Experimental work:

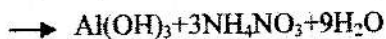
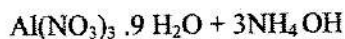
1-Raw materials:

Aluminum nitrate (Al (NO₃)₃.9H₂O, Hopkin and Williams), aqueous ammonia (1N), ethanol (fluka), hydrochloric acid (BDH) were all of analytical grade. Also commercial gamma alumina oxide (hopkin and Williams)

2-catalyst preparation:

The alumina hydroxide was prepared by added slowly one liter of ammonia solution (1 N) to the one liter of aluminum nitrate (1N) by titration with a continuous mixing at 90°C(water bath),to the point where the PH of the mixture reaches to a value of 7 . Aluminum hydroxide formed was left to settle for a period of 7-8 days to complete the precipitation and

agglomeration stage according to the reaction of:



It is then washed with hot distilled water and left for a bout 1.5 hr to allow for precipitation. The solution is then transferred to another container. The procedure of washing is repeated for several times. Aluminum hydroxide formed is in the form of past, it is very soft due to high percentage of humidity. It is therefore, dried at 110°C overnight with air. the samples were calcined in air at the required temperature (300 , 500 , 600 , 650 , 700 , 800 , 900 , 1000)°C for 6 hr . The calcined alumina oxide was crushed and then converted to powder (average particle size =500 μm) by ball mill and sieving machines.

3-thermal analysis:

In order to know the effect of temperature used to convert aluminum hydroxide into aluminum oxide. Thermal analysis was carried out for aluminum hydroxide using a Stanton Red Corof (TG 760 series). Curves were recorded simultaneously by placing a

sample in a platinum crucible and heated at a rate of 25 °C/min in a flow of atmospheric air. The temperatures range used was 25-1000 °C and the gas flow rate was 6 L/hr for all thermal measurement's thermal analysis was also carried out using DTA device from Hero's company (TA 500) with heating rate of 10 °C/min.

4-X-Ray diffraction:

The X-Ray diffraction of the catalysts were carried out using Philips X-Ray diffract meter with $\text{CuK}\alpha$ (wavelength 1.542 Å), 40 Kv and 20 mA. Radiation range of angles scanned was 10 to 70 on 2θ .

5-surfas area , pore volume and mean pore radius:

Surface area of the prepared catalysts were determined using BET technique by nitrogen adsorption at -196°C .The same system was employed to determine the pore volume and mean pore radius by the BJH method⁽¹⁴⁾.

6-Activity of the catalysts:

The activity of the catalysts were carried out in a tubular reactor ,operating under

atmospheric pressure and interfaced to a gas chromatography by a six-way sampling valve .A borosilicate glass reactor of 15 mm inside diameter and length of 200 mm was used , fitted with a thermo well and an electrically heated vertical tubular furnace . the reactor was packed with 0.15 gm of catalyst (500 μm) between two layers of glass-wool . The operating conditions of the reaction were, the temperature was 350°C and the flow rate of ethanol was 0.5 mol/hr over the catalyst bed by using metering pump and a preheater. The reaction products (ethylene, diethyl ether, water, and unreacted ethanol) were analyzed by gas chromatography using a 3mm x 2m stainless-steel column packed with 10% carbowax 20 M maintained at 90°C . A thermal conductivity detector and hydrogen as carrier gas at a flow rate of 40 cm^3/min were used. Conversion and selectivity are defined as⁽¹⁵⁾:

$$\text{Conversion} = \frac{\text{moles(ethanol)reacted}}{\text{moles(ethanol) fed}}$$

$$\text{Selectivity} = \frac{\text{moles}(\text{product}) \text{ produced}}{\text{moles}(\text{another}) \text{ produced}}$$

Results and Dissection:

Fig (1) shows the thermal analysis of aluminum hydroxide. The TG curve shows that the weight at 100°C reached 5% because of the loss of water molecules. DTG and DTA curves indicates the presence of a band at 265 °C, weight loss is measured at this temperature, using TG at an amount of 23.5%. This band shows loss of hydroxide ions.

Fig (2) shows the X-Ray diffraction for aluminum hydroxide heated at temperatures between 300-1000 °C . The d-spacing for each peak was calculated using the Bragg equation ⁽¹⁶⁾:

$$n\lambda = 2d \sin\theta$$

Where n = 1 (order diffraction)

$\lambda = 1.5418$ (wave length of X-Ray)

θ = diffraction angle

The 2 θ for all beaks are indicated on the X-Ray diffraction for all calcintion temperatures used and the calculated d-spacing shown on fig (2).

While table (1) shows the d-spacing and 2 θ standers of all types of alumina oxide ⁽¹⁷⁾.From the data on fig (2) and table (1) it could be shown that the aluminum hydroxide that heated at 300°C indicates the presence of alumina oxide crystals (defected crystals formed) . The band at 2 θ = 28.51 (d-spacing= 3.13) indicates the presence of boehmite as shown in table (1) ⁽¹⁷⁾. At calcination temperature of 500°C, more than 90% of γ -Al₂O₃ crystals are formed which is seen clearly at bands of d-spacing = 2.4, 1.97 and 1.4 A^o exacted the band of d-spacing = 2.7 A^o which may represents the presence of δ -Al₂O₃ as shown in table (1).While at calcination temperature of 700°C, it could be shown that the bands of γ -Al₂O₃ are seen much more clearly but at the same time the appearance of bands at d-spacing = 2.71 and 1.52 A^o could be explained in terms of δ -Al₂O₃ and θ -Al₂O₃ crystals respectively .The increase in the intensity of bands could be due to the increase in growth of crystals. As calcinations temperature increases in the range of 800 to 900°C, a new structure is formed which could be responsible for formation of crystal structure of θ -Al₂O₃ as shown in table (1) ⁽¹⁷⁾. Fig

(2) shows that at calcination temperature of 900 and 1000°C, the δ -Al₂O₃ crystal structure are formed which is non-reactive phase. From the results of X-Ray diffraction, it is concluded that γ -Al₂O₃ formed by heat treatment of aluminum hydroxide at temperatures ranging between 500 and 700°C contains γ -Al₂O₃ as a main constituent with a small percentage of the δ -Al₂O₃ and θ -Al₂O₃ crystals.

Fig (3) shows the X-Ray diffraction for aluminum hydroxide heated at calcination temperatures of 600 and 650°C. A similarity is noted in terms of crystal structure and degree of polymerization. Bands of 1.4, 1.97, 2.39 and 4.56 Å⁰ indicates the presence of γ -Al₂O₃ crystal also the band at 2.71 Å⁰ shows existence of a small amount of θ -Al₂O₃ or δ -Al₂O₃ phase as shown in table (1)⁽¹⁷⁾.

The surface area, total pore volume, and mean pore radius are shown in table (2) while the effect of the calcinations temperature on the activity of alumina oxide was expressed by the dehydration of ethanol at 350 °C. The analysis of the products of reaction using the prepared alumina oxide was shown in table (3) for all calcinations

temperatures used. The conversion of ethanol (calculated by using equation no. 1) as a function of calcinations temperature was shown in fig(4) and the selectivity for ethylene and diethyl ether(calculated by using equation no.2)versus the calcinations temperature of prepared alumina oxide was shown in fig(5) and fig(6) respectively. From figs (4, 5 and 6) it could be shown that the conversion of ethanol and the selectivity for ethylene and diethyl ether increases with increasing the calcination temperature of alumina oxide and reach to a maximum at (600-650) °C and then decreases with further increase in the calcinations temperatures of alumina oxide. This is may be due to that at the calcination temperatures (600-650) °C of alumina oxide, the active γ -Al₂O₃ peaks are seen much more clearly compared with other calcination temperatures used. Also at this calcinations temperature (600 – 650)°C, the surface area, total pore volume and mean pore radius are good compared with other catalysts that calcined at other temperatures used as shown in table (2).Table (2)show that the surface area of the catalyst increases with increasing the

calcination temperatures and reach to a maximum at (600-650)°C and then decreases with further increase in the calcinations temperatures of alumina oxide. This may be attributed to the fact that when increase the calcinations temperatures, the surface area of the catalyst increase as pores are formed and then decreases with further increase in the calcinations temperatures above 650 °C as a result of sintering phenomena and phase changes⁽⁹⁾ that occurs at higher temperatures. Therefore high surface area and high portion of γ -Al₂O₃ phase are reflected on the high catalyst activity of the catalyst that calcined at temperatures of 600 – 650°C.

In order to compare the activity of prepared alumina oxide with the activity of commercial alumina oxide, the dehydration of ethanol at 350°C was carried out using the commercial alumina oxide. The results indicated that the conversion of ethanol, the selectivity for ethylene and for diethyl ether were 93.57, 12.7, and 82.13 % respectively, while the conversion of ethanol, the selectivity for ethylene and diethyl ether were (94.71 and 95.97), (12.92 and 13.21), and (85.51 and 85.09) % when using

the calcined prepared alumina oxide at 600 and 650°C respectively. This indicates that the preparation procedure and calcinations temperature used satisfies the final goal of preparation of active γ -Al₂O₃ catalyst.

Conclusion:

The following conclusions could be drawn from the present investigation:

- 1- The calcination temperature influence on the type of crystal phase of alumina oxide products as shown in figs (2 and 3) and table (1).
- 2- It appears that there is a definite dependence of the activity and physical properties of the alumina oxide on the calcinations temperature as shown in tables (2 and 3) and figs (4, 5, and 6).
- 3- The best calcination temperatures of alumina oxide was 600-650°C. At this temperature, the prepared catalyst have a good characteristics compared with that obtained when used the commercial catalyst.

- 4- The conversion of ethanol and the selectivity for ethylene and diethyl ether increases with increasing the calcination temperature until a maximum value at 600-650°C and then decreases with increasing calcination temperature.

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Table (1) the d-spacing and 2θ stander of Aluminum hydroxide and alumina oxide⁽¹⁷⁾.

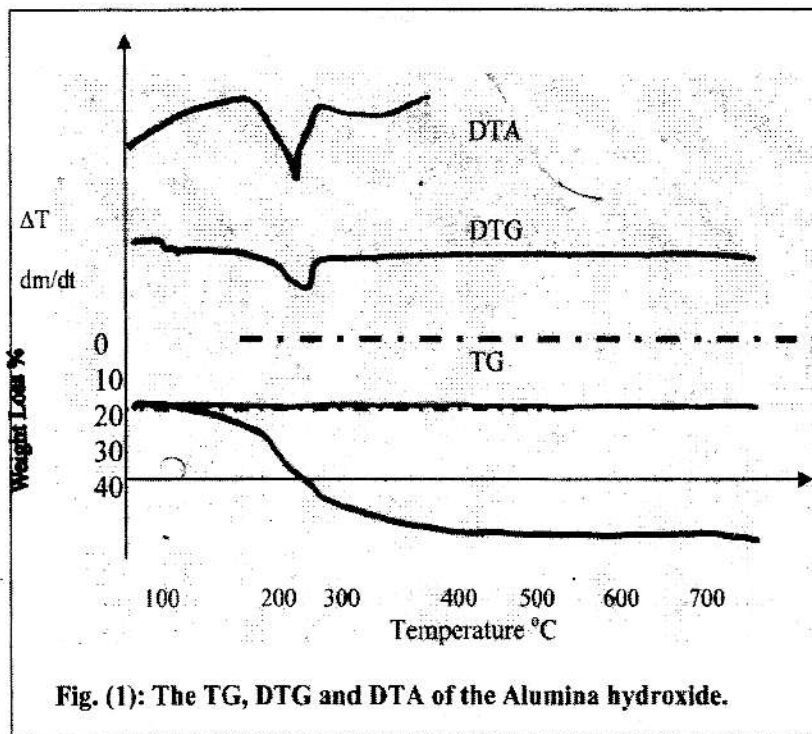
Gibbsite			B- Al(OH) ₃ Bayerite		
2θ	d(A°)	I/I ₀	2θ	d(A°)	I/I ₀
18.4	4.82	100	40.64	2.22	100
20.46	4.34	40	18.84	4.71	90
20.66	4.30	20	20.42	4.35	70
Boehmite			γ-Al ₂ O ₃		
2θ	d(A°)	I/I ₀	2θ	d(A°)	I/I ₀
14.49	6.11		45.90	1.977	100
28.52	3.13		37.63	2.39	80
			67.09	1.395	100
			39.52	2.28	50
			19.46	4.56	40
δ-Al ₂ O ₃			θ-Al ₂ O ₃		
2θ	d(A°)	I/I ₀	2θ	d(A°)	I/I ₀
46.57	1.95		67.366	1.39	100
46.07	1.97		32.93	2.72	80
33.053	2.71		31.386	2.85	80
			45.1	2.01	80
			60.07	1.54	60
			32.92	2.72	80
			41.02	2.2	30
κ-Al ₂ O ₃			α-Al ₂ O ₃		
2θ	d(A°)	I/I ₀	2θ	d(A°)	I/I ₀
67.336	1.93	100	43.69	2.085	100
34.91	2.57	80	57.56	1.601	80
42.858	2.11	80	35.16	2.552	90
45.58	1.99	40	25.604	3.479	75

Table (2) the physical properties of the alumina oxide with various calcination temperatures.

Calcination temp.(°C)	Surface area (m ² /gm)	Total pore volume (cm ³ /gm)	Mean pore radius (Å ⁰)
300	172	0.37	17
500	273	0.54	23
600	314	0.57	47
650	322	0.61	52
700	261	0.63	55
800	138	0.67	57
900	120	0.66	55
1000	117	0.68	58

Table (3) the mole percent products of dehydration of Ethanol for each calcination temperatures

Calcination temp.(°C)	Mol.% of Ethylene product	Mol.% of Diethyl ether product	Mol.% of water product	Mol.% of Unreacted Ethanol
300	3.952	37.727	18.110	40.210
500	8.136	61.443	15.170	15.250
600	12.24	80.99	1.48	5.29
650	12.678	81.661	1.631	4.030
700	10.12	60.64	19.27	9.97
800	7.867	46.812	23.211	22.110
900	5.795	30.930	26.175	31.100
1000	2.958	20.686	23.157	53.260



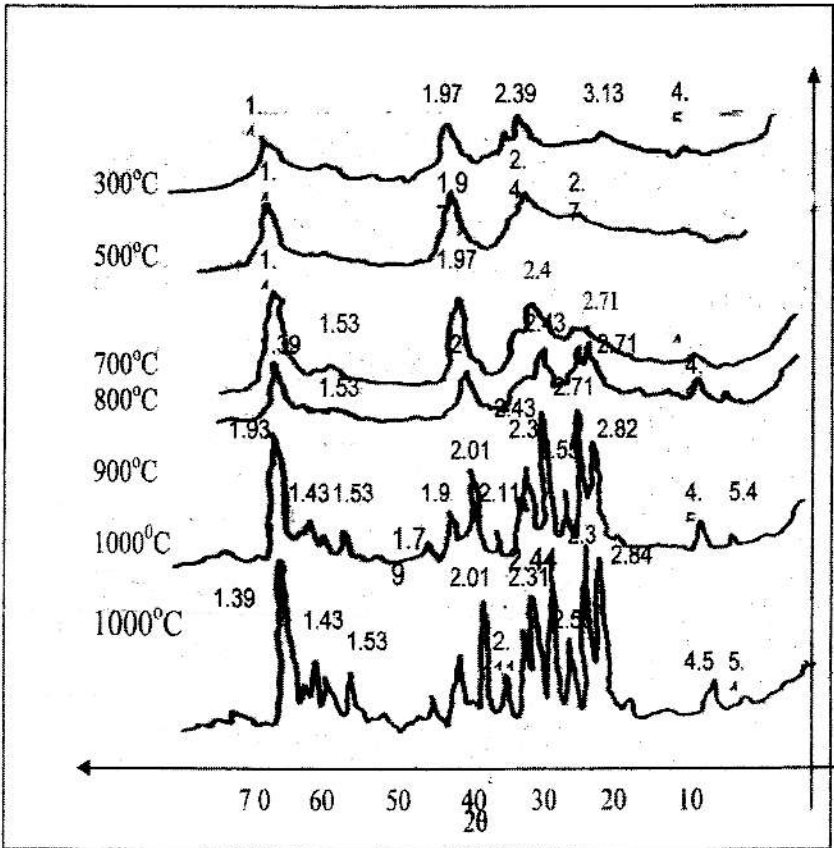


Fig. (2)The X-ray diffraction of Alumina Hydroxide with deferent temperatures

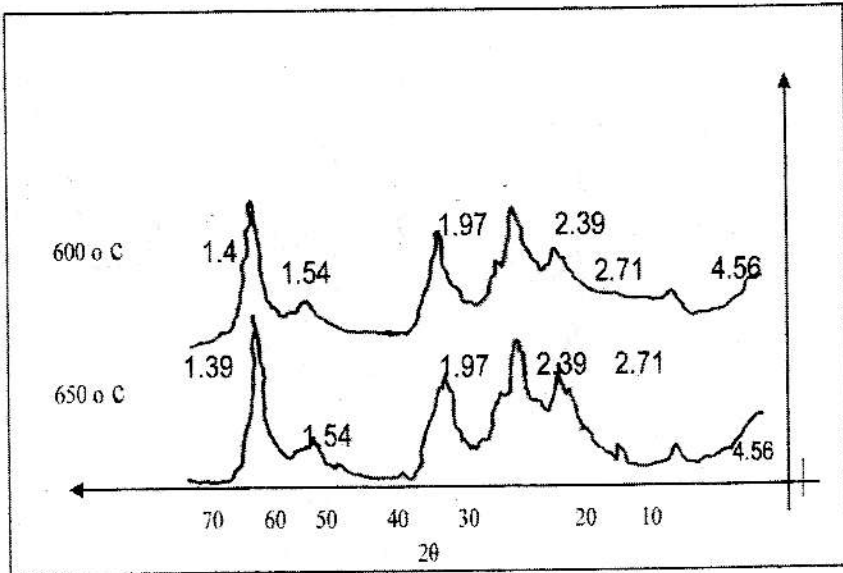


Fig. (3): The X-ray diffraction of Alumina Oxide at 600°C and 650°C.

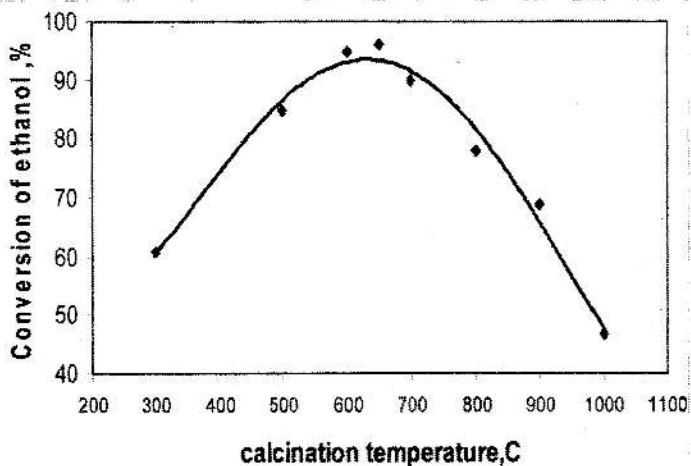


Fig (4) Conversion of ethanol versus the calcination temperature of Alumina oxide.

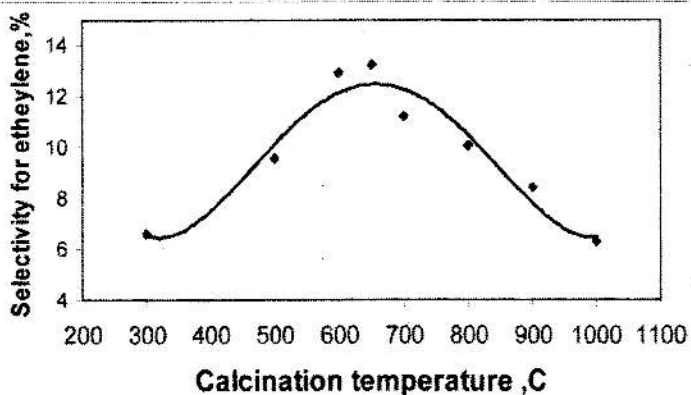


Fig (5) % selectivity for ethylene versus the calcination temperature of Alumina oxide.

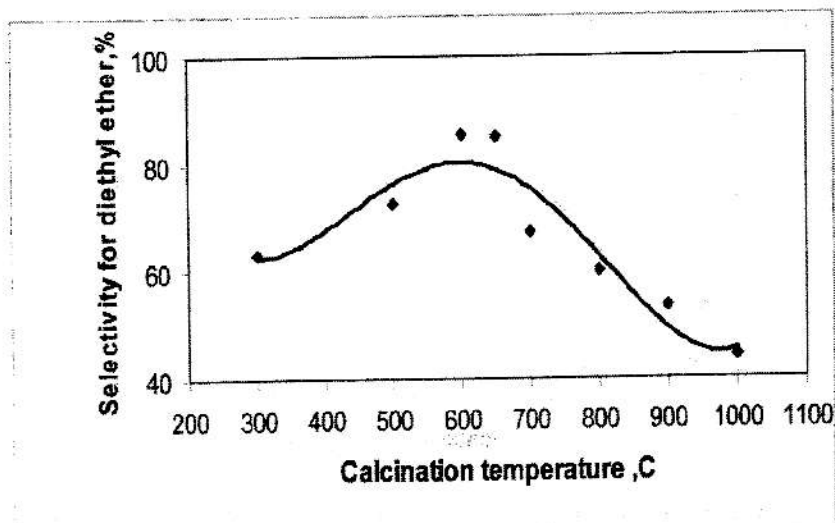


Fig (6) % selectivity for diethyl ether versus the calcination temperature of Alumina oxide.