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Extraction and Study of Properties of γ-Alumina Phase

R. R. A. AL-Ani
Department of Chemistry, College of Science, AL-Mustansiriya University

Abstract

Bauxite produced by AL-Gaar'a area containing (55.08 wt %) Al_2CO_3, used as row material for Gamma-alumina extraction by using the acidic method and acidic-basic method. The Gamma-alumina was identified by X-ray technique.

Two catalysts type Pt/alumina were prepared, one of them supported on extracted alumina (by this work) and the other was supported on commercial alumina, then compared the activity of these catalyst on hydro conversion reaction of n-heptane and its selectivity.

The catalyst prepared from extracted alumina showed a higher activity towards isomerization products, while the catalyst prepared from commercial alumina showed a higher activity towards cyclization products, also the results shows a similar behavior for both catalysts at different reaction conditions.

Introduction

Alumina metal is the third element on earth after oxygen and silicon. Kozmen (1) mentioned that there are (250) metal contain aluminum. The most important one is bauxite, kaoline, boehmite, diaspore and gibsite. The European bauxites contain around (90%) Al_2O_3, while the other bauxites between (40-55%) Al_2O_3 included the Iraqi bauxites (2).

The bauxites used mainly for producing of aluminum metal, as supporter for the catalyst, for thermal isolators, and for medicinal manufacturing (3).

The different aluminum phases (4,5) (γ, δ, κ, η, ρ, σ, χ, and α) can be prepared by removing water from the hydroxides $Al(OH)_3$ or $AlO(OH)$ in different temperatures.

The activity of adsorption and synsitization depend upon different factors (6,7), like the crystal structure, pore texture and surface feature, which are depend on the way of removing water from metal hydroxide.

The most active phase is the γ-alumina (8) due to high surface area, number of pores and contains an acidic oxygen atoms.

This work deals with preparation of γ-alumina by using an Iraqi bauxite as a raw material and used it as a supporter for catalyst.

Experimental

Bauxite, kaoline and lime stone were supplied from Gaar'a, and Dewekhala region (table 1).

All the chemicals used were commercial grade without any further purification, and were supplied from (B.D.H.) and (Fluka) chemicals.

❖ Instruments

1. Grinder RETCH-No. 2482.
2. Oven BS, model-ov. 330.
3. Muffle Furnace Lmf-3. Carbolite.
4. Single screw extruder LA 31 Truder.
5. Grushing strength ERWEKA-TBH 28.
6. Hydrogenation Unit Reactor-Geo-Mechanics, French Company.
7. Pressure Reactor-Stainless Steel, Volume 23 cm^3, Teflon Coated, Bochi.
8. Gas Chromatographic Analysis, PYE-Unicum 304.
9. Laser partical size (analysette-22).
10. X-ray difraction, Philips difractometer-220.

❖ Production of alumina using acidic method (8,9)

The extraction method of alumina was carried out using bauxite (Gaar'a) as a raw material in different stages:

1. Preparation of raw material for extraction:

In this stage the raw material was grinded using a grinder to get a suitable particle size (50 µm). After that the material was washed with distilled water several times, decantation and dried at (110 °C) for (3-4) hours. The dried material was grinded again.

Four samples were prepared from the dried material and the calcination process was carried out at different temperatures for each sample (650-950 °C) for (6) hours each. After the burning process, the samples were grinded again to make it ready for next stage.

2. Digestion process using hydrochloric acid:

A sample of (6.5 gm) from the first stage material was loaded in the pressure reactor and (13.5 ml) of HCl in different concentrations (29.5-35.5 %) was added, closed the reactor vessel and was heated by silicon oil bath (b.p. 315 °C).

A series of experiments were carried out to extract the alumina with HCl. For each experiment a different temperature (160-220 °C), pressure (4-12 Bar) and different reaction time (60-180 min) were accomplished.

The reaction mixture was cooled, filtered and transferred to next stage (table 2).

3. Precipitation:

Aluminum hydroxide precipitation process was accomplished by slow addition of ammonia solution (25 % NH_4OH) with stirring to the mixture. A white precipitate appeared in the mixture, the ammonium addition continued with checking the mixture pH, when the pH of the mixture reached (8.5-9.5) the addition stopped, the mixture left for (1) hour with stirring at (80 °C), cooled, filtered and the precipitate was washed with distilled water, transferred to the forth stage.

4. Drying and calcination:

The precipitate from last stage was dried at (120 °C) for (2) hours and transferred to muffle furnace for calcination process, the temperature was rise gradually to (650 °C) during (6) hours (table 3). After the temperature reached (450 °C), a sample of produced alumina was taken each (150 °C) for identification of alumina phases by X-ray diffraction (Fig. 1, 2, 3,4).

- **Production of alumina by acidic-basic method:**

Extraction of alumina using acidic-basic method was carried out in two stages. The first stage included the extraction of alumina using polish method (10) and the second stage was the digestion of aluminum trihydrate using HCl to get highly pure alumina:

1. **Extraction of alumina using polish method:**

To get the alumina trihydrate (Dewechala) kaoline and calcium carbonate (lime stone) from Kelo-160 region was used.

A. Kaoline (45 µm particle size) and $CaCO_3$ was mixed (3:1). The mixture was calcinated at (1350 °C) for (6) hours. The mixture was left to cool then grinded in electric grinder.

B. The resulting powder from above stage (45 µm particle size) was added to $CaCO_3$ solution (6 %) at (90 °C) for (1) hour with mixing. The dissolved solution was decanted to separate undissolved solid.

C. The solution (sodium alumina with dissolved silica) was mixed with calcium hydroxide (2 %) at (98 °C) for (30) minutes with mixing. The silicate was precipitated as aluminum-calcium silicate, and removed by filtration.

D. The remaining solution was heated to (70 °C), CO_2 gas was bubbling through solution with mixing for (1) hour. Aluminum hydroxide was precipitated as gelatin. The resulting gelatin was calcinated between (150-550 °C) for (5) hours. Analysis of the product (aluminum oxide) showed a percentage of (80.43 %) aluminum oxide.

2. **Digestion with hydrochloric acid:**

The digestion of aluminum oxide (trihydrate) was accomplished by adding (3.2 ml) of (32.5 %) HCl to (6.5 gm) of aluminum oxide from the last stage in (23 cm^3) volume pressure reaction vessel. The pressure vessel was put in oil bath after closed tightly and the temperature was raised gradually to (200 °C) and (10 bar) pressure for (2) hours.

The reaction vessel was left for cooling, the solution was filtrate and aluminum chloride solution was transferred to a conical flask. Ammonia solution (25 %) was added with stirring during (30) minutes , aluminum hydroxide was precipitated (at $pH = 9$), the mixture was left for stirring for another (1) hour at (80 °C), cooled to room temperature, filtered and washed with distilled water.

The aluminum hydroxide was dried at (120 °C) for (2) hours, and the aluminum oxide was calcinated at (150-550 °C) for (5) hours.

A sample of calcinated Al_2O_3 was taken and analyzed for purity, (90.53 %) aluminum oxide was gained.

❖ Determination of chloride concentration (11):

The chloride ion in alumina samples was determined using Volhard method (11).

The method depends on silver nitrate solution (30 ml , 0.05 N) added to (0.05 gm) of alumina sample in (30 ml) distilled water with (5 ml, 6 N) nitric acid. The silver halogen was precipitated and the excess concentration of silver nitrate were titrated against ammonium thiocyanate (NH_4SCN, 0.05 N), silver thiocyanate precipitated as faint reddish precipitate.

$$Ag^+ + SCN^- \longrightarrow AgSCN \downarrow$$

The concentration of chloride ion was calculated using the equation:

$M_{Cl} = M_{AgNO3} - M_{NH4SCN}$

❖ Formilation of alumina:

1. **Formilation by extruders**:

The alumina was formilated as cylindrical bars by using a single screw extruder, as following:

(20 ml) of distilled water was added to (100 gm) of prepared alumina (45 μm particle size) and (3 gm) of kaoline (binder) (45 μm particle size) with mixing. The homogeneous mixture at (40 °C) was left for (24) hours, and then the extruder was used to get a (3 mm) radial cylindrical bars, which cut to (5 mm) long bars, dried at (120 °C) for (2) hours, and calcinated at (550 °C) for (5) hours and left in dissicator.

2. **Formilation by tableting machine**:

The same alumina paste was used as in (1). Rotary press Y.Y. 0221-1995 machine was used to shaping the alumina as tablets.

A pressure of (20 atm) was used to prepare (0.7 × 0.4 cm) tablets, dried at (120 °C) for (2) hours, calcinated at (550 °C) for (5) hours and left in dissicator.

3. **Formilation by bendates**:

The shaping of alumina as beds was accomplished by using SP. 0222-1995 Rotary distributor.

Poly vinyl alcohol (PVA) (35 μm particle size) was used as a binder, (0.6 gm) of the binder was added gradually to the alumina (20 gm) with mixing and were backed in the machine. The machine was set at (180) cycle/min. The alumina was thrown the sphericals of the alumina to the collecting vessel, then dried and calcinated.

❖ Preparation of Pt/Al_2O_3 catalyst (0.35 % Pt):

(20 gm) of the catalyst Pt/Al_2O_3 was prepared by using commercial active alumina (CA-S) (S.A. = 180 m^2/gm, P.V. = 0.55 cm^3/gm) as a spherical and (20 gm) of catalyst Pt/Al_2O_3 (0.35 % Pt) as extracted alumina (by this study) EA. S. (S.A. = 190 m^2/gm, P.V. = 0.55 cm^3/gm) as extrudates.

In the first stage the air was expelled from the pores of the supporter by using vacuum system then the pores were saturated by solution of metal salt (H_2PtCl_6) (40 % Pt) by Impregnation method (12).

❖ Impregnation method:

(0.1756 gm) of metal salt (H_2PtCl_6) was dissolved in (11.5 ml) of deionized water; added to (20 gm) of the commercial alumina as extrudate alumina and left over night, dried at (120 °C) for (10) hours, and calcinated at (550 °C) for (5) hours (in the presence of dry air) to convert the metal salt to metal oxide.

The prepared catalyst was reduced by hydrogen gas at (350 °C) for (3) hours.

❖ Physical properties of extracted alumina and the catalyst:

1. Bulk density:

The bulk density was measured by taking a certain quantity of the supporter (or catalyst) and was put in a cylindrical vessel of (2 cm) diameter. The difference between the empty cylinder and filled one with catalyst or supporter was used in the following equation, (table 3):

$$\rho = \frac{w_2 - w_1}{v}$$

Where:

ρ = bulk density
w_1 = empty cylinder
w_2 = filled cylinder
v = volume of material

2. Apparent porosity:

A sample of the extracted alumina as the catalyst was weight after dried in oven for (120) minutes at (250 °C) (w_1). The sample was put in a boiling water for (5) minutes, then left to cool for (10) minutes, dried by smooth paper and weight (w_2). The (w_3) was determined by weight an sample hanged in cold water by a stainless steel boat using sensitive electronic balance (4-digits) (table 6).

$$\rho_a = \frac{w_2 - w_1}{w_2 - w_3}$$

Where:

ρ_a = apparent porosity

3. Laser particle size measurements:

The particle size of the alumina and the catalyst was measured by using analysette-22. The samples were used as a suspension in the measurement cell. The particle size, which was measured by instruments was (0.16-1160 µm) during (2) minutes time.

4. Surface area measurements:

The surface area was measured by Bet-isotherm using micrometric ASAP-2400 instrument and IBM-PC/TX computer. The program of the computer used the Bet-isotherm equation:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} (P / P_o)$$

Where:

V = adsorbed gas at equilibrium pressure (P)

V_m = gas volume, which cover one layer of the surface (slope)

P_o = gas pressure at saturation at (T) temperature

C = constant depends on adsorbate and absorbent (intercept)

A straight line was get by drawing [$P / V(P_o - P)$] against (P / P_o). the experimental temperature was (-196 °C).

The surface area measured by (m^2) as in the following equation:

$$S.A. = \frac{V_m}{22400} \times a_m \times N \times 10^{-20}$$

Where:

a_m = molecule surface area (one layer) (0.162 nm^2)
N = Avocadro's number

5. Crushing strength:

The crushing strength of the catalyst and the supporter were examined by using [ERWEKA-TBH 28] instrument. The measurement was carried out for (10) samples for each kind of catalyst and supporter using the following equation (table 6):

$$\overline{X} = \frac{\Sigma X}{n}$$

Where:

$\overline{X}$ = average crushing strength
ΣX = crushing strength values (Newton units)
n = number of samples

6. Activity of prepared catalyst (Pt/Al_2O_3):

Laboratory hydrogenation unit (Ruska instruments corporation MPL-Houston) was used to measure the activity of the catalyst.

The reactor was packed with (20 cm^3) of commercial catalyst in the first experiment and (20 cm^3) of prepared catalyst in the second time. The catalysts were packed between two layers of spherical glass. The reactor was heated by steel jacket heater, controlled by thermocouples.

The heptane gas was pumped by a feed pump to the reactor after it was mixed with hydrogen gas under pressure in a rate of (1 cm^3/min). The reaction mixtures were pushed through the catalyst (as peads, cylindrical extruder), the products were cooled by alcohol condenser. The condensed liquids were collected in a separating funnel, and the gases were pureed through a gasmeter. The reaction temperature was (325-400 °C), and the pressure was (10 bar) (H_2 partial pressure). The molar ratio of hydrogen gas to heptane was (3:1).

7. Gas chromatography analysis:

(Vista varian 6000) was used for testing, using flame ionization detector and (10 %) Apesond chromosorb W, 60-80 mesh column of (2.5 m) long and (2 mm) diameter.

The percentage of the products was calculated by the following equation:

$$\% \text{ Conversion (CN)} = \frac{nA_o - nA}{nA_o} \times 100$$

Where:
nA_o = initial concentration of heptane
nA = concentration of heptane at (t) time

The percentage of product of isomerization, cyclization and decomposition of heptane was calculated by the following equation:

$$\% \text{ Percentage yield} = \frac{n_i}{nA_o} \times 100$$

Where:
n_i = number of total moles of products

The selectivity (Si) was calculated by the following equation:

$$\% \text{ Si} = \frac{n_i}{nA_o - nA} \times 100$$

The results of chromatography analysis were listed in tables (27-3 – 24-3].

Results and Discussion

❖ Ore contents:

In this study bauxite was used as an alumina ore from AL-Gaar'a area to extract aluminum oxide. Bauxite ore, which contains (55.08 %) of alumina, the X-ray diffraction analysis shows it contains Kaoline and bauxite mainly (table 1). In addition to bauxite, kaoline (Dewekhala) was used in extraction of alumina, which consists mainly of silica, alumina and oxides of titanium and iron (table 2).

❖ Results of extraction processes:

The bauxite ore was grind to (50 µm) and was washed several times with distilled water to get red of salts, dried and grinned again.

❖ Calcination temperature:

The calcination of bauxite was accomplished using four different temperatures (650, 750, 850 and 950 °C) before extraction processes. The alumina percentage was increased by increasing of calcination temperature (Fig. 1-3, 2-3) (table 1-3). The increasing of alumina percentage is due to two factors. The first was the weakening of the bonds between silica and alumina, which make the acid in the next step more effective to break those bonds. And the second factor was to control the transformation between the alumina phases to produce (γ) phase alone.

Fig. (2-3) shows that the best calcination temperature was (950 °C), which produced a higher γ-alumina content. On the other hand, the difference between results of (950 °C) calcination temperature and (850 °C) was very low, then the temperature which was chosen as a best calcination temperature was (850 °C) as matter of energy saving.

❖ Effect of reaction temperature:

The digestion with acid was carried out at temperature range (160-220 °C), table (4).

Aluminum hydroxides, which produced by the action of acid on bauxite in a pressure reactor and alternatively aluminum oxide produced, were increased by increasing reaction temperature, which reached (54.5 %) at (200 °C).

The increasing of reaction mixture temperature leads to increase the pressure of the reactor vessel. The temperature and the pressure increased the dissolving of the alumina in acid solution (12).

Many complex reactions take place in these conditions, the main reaction is between acid and Al_2O_3, which was presence in many formulas like γ-AlO(OH), α-$Al(OH)_3$. In the same time other reactions take place between the acid and other oxides of iron and titanium (13). This processes lead to get an alumina, which contaminated with other oxides, table (4).

❖ Acidic function (pH) effect:

The pH effect was studied by using different pH ranges (8-9.5) and precipitation process using ammonium hydroxide (25 % NH_3).

The pH range chosen depending on literature (13,14). By this pH ranges, we can get the best yield of Gibsite α-$Al_2O_3.3H_2O$ and bohmite α-$Al_2O_3.H_2O$, which is lead to γ-alumina.

Table (3-3) shows that the increasing of basisty leads to increasing of aluminum hydroxide produced by precipitation. The best products was at pH = 9 (15).

Henrik (16), in his study showed that the precipitation process occurs when the hydroxide was added to aluminum salt solution at pH range between (9-9.5). this is due to the low solubility of aluminum hydroxide in this pH range. The references mentioned that the mechanism of the reaction was unknown apart from the product $Al(OH)_3$.

$$AlCl_3 + 3NH_3 + 3H_2O \longrightarrow Al(OH)_3 + 3NH_4Cl$$

The same effect of pH (8-9.5) was noticed on aluminum oxide product after calcination at (450-650 °C) (table 3-8, 3-6). Calcination of aluminum hydroxide to produce active alumina in high yield (59.21%) by using pH = 9.5 and calcination temperature (650 °C) was the best results (table 7-3).

The calcination process leads to transformation of alumina trihydrate to alumina monohydrate and then to Al_2O_3 in different phases depending on calcination temperature starting material, and reaction conditions (17,18) as following:

$$Al_2O_3.3H_2O \xrightarrow{\Delta} Al_2O_3.H_2O + 2H_2O$$

$$Al_2O_3.H_2O \xrightarrow{\Delta} Al_2O_3 + H_2O$$

❖ Effect of pH on surface area and particle size of aluminum oxide:

The study of pH effect on surface area and particle size of the produced aluminum oxide was accomplished after the calcination processes (550 °C). Table (8) shows that the surface area was increased by increasing the basisty of the medium and reached the highest value at pH = 9 (203.6 m^2gm^{-1}), then decreased by increasing the pH. On the other hand, the particle size of alumina produced using the same temperature decreased by increasing basisty (pH) and reached a lowest value at pH = 9 (average of 9.14 μm) and then increased by increasing pH.

The increasing in particle size of alumina due to the agglomeration during the precipitation processes by the build up of the crystal size or break down of the others. These results were much like the results of Tschamper (19), which mentioned that the (S.A.) of (Al_2O_3) decreased by increasing of particle size and the best result was produced at pH = 9 and calcination temperature of (550 °C), table (5).

❖ Effect of HCl concentration on extraction processes:

A number of different concentrations of HCl solutions were prepared (29.5-35.3 %) for digestion processes.

The increasing of HCl solution concentration dissolved more alumina in addition to ferric, titanium, calcium and magnesium oxides, which produced a contaminated alumina.

Table (10-3) shows an increasing in alumina produced by increasing of HCl solution concentration (32.5 %). After this concentration (32.5 %), the difference in alumina production level low.

On the other hand, the effect of acid which was used in the digestion processes on the surface area of alumina after calcination was studied. Table (9) shows the alumina surface area decreased by increasing of acid concentration. The best area which was produced by the acting of acid of (29.5 %) concentration (205.74 m^2gm^{-1}), then the area started to decrease by increasing of acid concentration and reduced (162.6 m^2gm^{-1}) at acid concentration of (35.5 %). The decreasing of the area was due to increasing of chloride ion which increased with acid concentration increasing.

The decreasing of the surface area by increasing of chloride ions may be due to the contamination of the pores by chloride ions, which made the alumina less porosity and then less surface area. All these factors pointed that the acid concentration (32.5 %) was the best acid concentration used that the produced alumina surface area was (203.6 m^2gm^{-1}) at (32.5 %) concentration, table (3-11).

❖ Effect of reaction time on extraction products:

The effect of reaction time was followed by checking of the acid concentrations through the reaction. It is clear that there was increasing in producing aluminum hydroxide and then the aluminum oxide (after calcination) with longer reaction time. This increasing in products were lower after the reaction time passed (120) minutes (table 10).

This reaction time excluded the time taken to reach reaction temperature (2.5-3) hours. Then the reaction time which was chosen was (120) minutes as a perfect time to get a best product (12).

❖ Extraction of alumina by acid-base method:

Extraction processes of alumina hydroxide by acid method was lead to dissolved a lot of metal oxides. This metal oxide produced a pure aluminum oxide. This problem solved by using the basic method (Payer method), which used for bauxite that contains less silica as the polish method (Curzmick) which depend on heating kaoline and bauxite as a starting material with calcium carbonate at high temperature (1350 °C).

The mixture was digested with sodium carbonate at (90 °C) to produce sodium alumina with some impurities of silica which removed by calcium hydroxide to get a pure product of sodium alumina. The sodium hydroxide was precipitated by passing CO_2 gas through the mixture.

The aluminum hydroxide produced was calcinated to aluminum oxide. The aluminum oxide which produced contained an impurities, the aluminum oxide digested by (32.5%) hydrochloric acid to get aluminum chloride which reacted with (25%) NH_3 to get highly pure aluminum hydroxide.

The chemical analysis of both products of Payer method and the acid-base method shown the purity of aluminum rase from (85.43%) to (90.53%).

The acid-base method can be used to extract the alumina from the highly contain silica as kaoline which is available in the west desert of Iraq.

❖ Formation processes:

The γ-alumina (extracted) was formed in different shapes at different conditions to choose the best shape to use it as a supporter for the catalyst Pt/alumina depending on the physical and mechanical properties.

The γ-alumina was formed as extrudates, beads and pellets. The most important factors that effect the forming process were the particle size, binding materials, percentage of binding materials and water content.

To choose the best shape of alumina suitable for a reaction done depending on activity, mechanical resistance and the kind of reactor used (20).

Many examinations were done for each shape of the γ-alumina -extrudates, beads and pellets- (table 11), as the crushing strength (depending on the binder), surface area and the particle size (table 11).

Poly vinyl alcohol (PVA) was used as a binder for the formation of γ-alumina (3%) which gave a good macropores and a reasonable crushing strength as shown in table (11).

❖ X-ray diffraction of phases identification:

Identification of γ-alumina phase using X-ray diffraction (Fig. A2) was accomplished after calcination at (45 °C). Fig. A3 shows the γ-alumina phase which calcinated at (550 °C), and Fig. A4 shows the γ-alumina phase by using acid-base method at (550 °C) calcination temperature.

❖ Activity measurements of the catalyst Pt/Al_2O_3:

Two catalysts were used in reforming reactions of normal heptane, the first catalyst was prepared by this study and the second one was Pt/Al_2O_3, which supported by commercial alumina (CA-S). The effects of the reaction conditions on the products and reaction selectivity were studied by using catalyst (EA-S and CA-S). The activity of catalysts were measured at different temperatures (325, 400 °C) and a partial hydrogen gas presure (10 bar) and the molar percentage of hydrogen gas to heptane [H_2/He = 3.0].

Table (12) shows an increasing in heptane reforming in presence of hydrogen gas by increasing of reaction temperature and reached (41.45%) at (400 °C) by using the catalyst (CA-S). On the other hand, a same effect was noticed for the (EA-S) catalyst that the reforming of heptane reached (42.86%) at (400 °C), table (14).

From the information in table 12 and 14 a slow increasing in heptane reforming was noticed for both (CA-S and EA-S) catalysts by increasing temperature, which is due to other reaction conditions like hydrogen pressure (P_H) and gas vacuum speed (LHSV) in addition to reaction temperature. The (P_H) has an effect on the active sites of the catalyst (competition) between hydrogen and heptane. On the other hand, the (LHSV) has an effect on products that along the time of the contact between reactants and the catalysts.

By compering both results of reactions by using (CA-S and EA-S) catalysts, it can be concluded that the extracted alumina (EA-S) produced a higher percentage in reforming of heptane than that of usin (CA-S), table (26-3).

❖ Selectivity of catalysts (EA-S and CA-S) for isomerization and fragmentation reactions:

The study of selectivity of catalysts (CA-S and EA-S) for isomerization and fragmentation reactions of hydrocarbones shows that at low temperatures (below 350 °C), the isomerization products were a result of controlled reactions and by increasing reaction temperature higher than (375 °C) the fragmentation products increase as a result of fragmentation controlled reactions (tables 13 and 15).

This was due to selectivity of both catalysts towards the products of isomerization and fragmentation reactions. This behavior of the catalysts (CA-S and EA-S) were due to two reasons:

1. The desorption of hydrocarbones from the strong acidic positions was hindered.
2. The fragmentation products were explained as a result of both methyl hexane and dimethyl pentane in addition to hexane itself.

On the other hand, both catalysts (CA-S and EA-S) act in a same way that the dehydrogenation and cyclization products were increased by increasing the reaction temperature, and when the reaction temperature reduced (350 °C) those products decreased by raising the reaction temperature. The lowest value for the cyclization and dehydrogenation reactions were at reaction temperature (400 °C), which is (2.0114%). On the other hand, the products of fragmentation reaction were raised by increasing the reaction temperature. The highest fragmentation products were got at (400 °C) (12.56%), (tables 11 and 13).

The behavior of both catalysts towards the cyclization and dehydrogenation products depends on many factors. The reaction temperature, hydrogen partial pressure, permitimity and metal dispersion on supported substance.

The metal dispersion of alumina plays very important act in cyclization and dehydrogenation reactions as mentioned in many previous studies (21,22).

Conclusions

The conclusions of this study built on two parts.; the extraction of γ-alumina and forming of this alumina as a first stage. The second stage was using this extracted γ-alumina as a supporter for Pt catalyst (Pt/Al_2O_3), and measurement of the prepared catalyst in reforming of heptane in presence of hydrogen gas.

1. In the first stage, bauxite (Gaar'a) was chosed as a good one for γ-alumina extraction because of the high percentage of alumina. The best concentration of HCl for digestion was (32.5%), the best reaction temperature was (200 °C), reaction time of digestion was (120 min), reaction pH was (9.0) and calcination temperature was (550 °C).

   The extracted γ-alumina purity can be improved by using acid-base method when using raw material of high contents of silica as Dewekhala kaoline.

   In the formation process of extracted γ-alumina, the extrudates gave the best active alumina by using kaoline (3%) as a binder.
2. In the second stage, the study of activity and selectivity of prepared and commercial catalyst show a similar behavior by using the same conditions in reforming of heptane.

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Table (1) Bauxite (Gaar'a) and Kaoline (Dewekhala) chemical analysis

Bauxite	Al_2O_3	SiO_2	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	MgO	L.O.I.
Wt %	55.08	24.4	2.8	0.8	1.7	-	-	0.41	14.81
Kaoline	Al_2O_3	SiO_2	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	MgO	L.O.I.
Wt %	33.40	48.98	0.28	1.24	1.07	0.40	0.30	0.27	14.06

Table (2) Effect of pH on aluminum hydroxide as a product

pH of reaction mixture	Dry aluminum hydroxide		
	Weight (gm)	Relative to alumina in bauxite	Relative to bauxite (wt %)
8.0	2.14	59.77	32.92
8.5	2.45	68.43	37.69
9.0	2.63	73.45	40.46
9.5	2.68	74.85	41.23

Table (3) Calcination temperature effect on extraction product

Calcination temp. (°C)	$Al(OH)_3$ produced after drying			Al_2O_3 produced after calcination		
	Weight (gm)	Relative to bauxite (wt %)	Relative to alumina in bauxite (wt %)	Weight (gm)	Relative to bauxite (wt %)	Relative to alumina in bauxite (wt %)
650	1.60	24.61	44.95	1.38	21.23	38.55
750	2.29	35.23	64.12	1.87	28.76	52.34
850	2.63	40.46	73.45	1.95	30.00	54.47
950	2.70	41.53	75.63	2.11	32.46	58.93

Table (4) Temperature effect on products of extraction process

Calcination temp. (°C)	$Al(OH)_3$ produced after drying			Al_2O_3 produced after calcination		
	Weight (gm)	Relative to bauxite (wt %)	Relative to alumina in bauxite (wt %)	Weight (gm)	Relative to bauxite (wt %)	Relative to alumina in bauxite (wt %)
160	1.08	16.61	30.16	0.48	7.38	13.40
170	1.38	21.20	38.55	0.70	12.15	22.06
180	1.85	28.46	51.67	1.21	18.61	33.79
190	2.36	36.30	65.91	1.57	24.15	43.85
200	2.63	40.46	73.45	1.95	30.00	54.47
210	2.67	41.07	74.57	1.96	30.15	54.74
220	2.69	41.38	75.13	1.98	30.46	55.30

Table (5) pH effect on produced alumina at 450 °C

pH	Al_2O_3 after calcination		
	Weight (gm)	Relative to alumina in bauxite (wt %)	Relative to bauxite (wt %)
8.0	1.62	45.24	24.92
8.5	1.84	51.39	28.30
9.0	2.05	57.39	31.53
9.5	2.12	59.21	32.61

Table (6) pH effect on produced alumina at 550 °C

pH	Al_2O_3 after calcination		
	Weight (gm)	Relative to alumina in bauxite (wt %)	Relative to bauxite (wt %)
8.0	1.54	43.01	23.69
8.5	1.79	49.49	27.53
9.0	1.95	54.47	30.00
9.5	2.07	57.81	31.92

Table (7) pH effect on produced alumina at 650 °C

pH	Al_2O_3 after calcination		
	Weight (gm)	Relative to alumina in bauxite (wt %)	Relative to bauxite (wt %)
8.0	1.46	40.77	22.46
8.5	1.70	47.48	26.15
9.0	1.86	51.95	28.61
9.5	2.01	56.14	30.92

Table (8) pH effect on surface area

PH	Surface area ($m^2.gm^{-1}$)	Average article size (μm)
8.0	152.30	26.43
8.5	183.01	13.12
9.0	203.60	9.14
9.5	185.12	9.84

Table (9) Effect of HCl concentration on extraction products

Acid conc. (w/v %)	$Al(OH)_3$ after drying			Al_2O_3 after calcination		
	Weight (gm)	Relative to bauxite (wt %)	Alumina relative to bauxite (wt %)	Weight (gm)	Relative to bauxite (wt %)	Alumina relative to bauxite (wt %)
29.5	2.05	31.53	57.25	1.10	16.92	30.72
31.0	2.49	38.30	69.54	1.60	24.61	44.69
32.5	2.63	40.46	73.45	1.95	30.00	54.47
34.0	2.66	40.92	74.29	1.97	30.30	55.02
35.5	2.71	41.69	75.56	2.01	30.92	56.14

Table (10) Effect of reaction time on extraction products

Reaction time (min)	$Al(OH)_3$ after drying			Al_2O_3 after calcination		
	Weight (gm)	Relative to bauxite (wt %)	Alumina relative to bauxite (wt %)	Weight (gm)	Relative to bauxite (wt %)	Alumina relative to bauxite (wt %)
60	1.95	30.00	54.46	1.35	20.76	37.70
90	2.56	39.38	71.50	1.67	25.69	46.64
120	2.63	40.46	73.45	1.95	30.00	54.47
150	2.72	41.48	75.97	2.00	30.76	55.86
180	2.74	42.15	76.53	2.03	31.23	56.70

Table (11) Physical and mechanical properties of support and catalyst

Physical and mechanical properties of support and catalyst	Alumina pellets (extracted) (0.7×0.4 cm)	Alumina extrudates (extracted) (0.3×0.5 cm)	Alumina spherical (commercial) (0.2 cm)	Catalyst supported on alumina extrudates	Catalyst supported on spherical alumina
Crushing strength	9.40	30.00	78.00	31.40	81.00
Bulk density (gm/cm^3)	0.70	0.710	0.696	0.720	0.723
Apparent porosity %	47.50	55.38	64.14	56.99	62.75

Table (12) Products of reforming process using catalyst supported by commercial alumina (CA-S)

Temperature °C	Conversion % n-heptane	Iso-products %	Cycle-products %	Crack-products %
325	27.503	17.301	2.571	7.631
350	37.049	24.481	3.101	9.467
375	37.288	24.704	2.050	10.534
400	41.452	26.878	2.014	12.560

Table (13) Selectivity of catalyst supported by commercial alumina (CA-S)

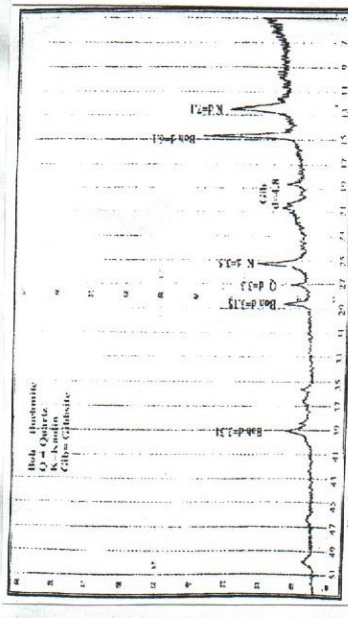
Temperature °C	Isomerization selectivity	Cyclization selectivity	Cracking selectivity
325	62.90	9.35	27.75
350	66.08	8.37	25.55
375	66.25	5.50	28.25
400	64.84	4.85	30.31

Table (14) Products of n-heptane reforming process using catalyst supported on extracted alumina (EA-S)

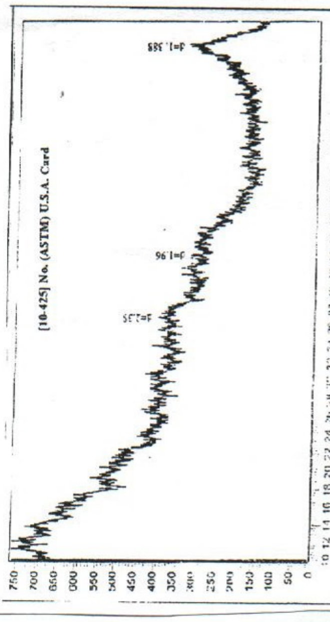
Temperature °C	Conversion % n-heptane	Iso-products %	Cycle-products %	Crack-products %
325	21.491	12.566	1.171	7.754
350	37.723	25.544	2.028	10.151
375	38.696	26.453	1.232	11.011
400	42.860	27.044	1.050	14.765

Table (15) Selectivity of catalyst supported on extracted alumina (EA-S)

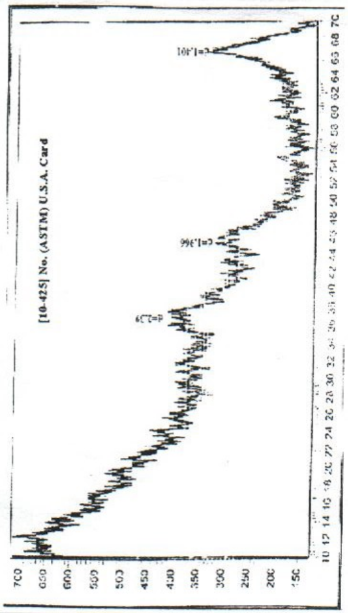
Temperature °C	Isomerization selectivity	Cyclization selectivity	Cracking selectivity
325	58.47	5.45	36.08
350	67.71	5.38	26.91
375	68.36	3.18	28.46
400	63.10	2.45	34.45



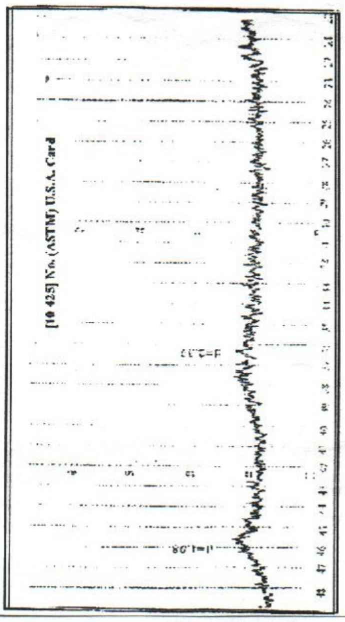
(A1): X-ray diffraction of bauxite (Gaar'a)



(A2): γ-Alumina produced at 650 °C



(A3): γ-Alumina produced at 950 °C



(A4): γ-Alumina produced by acid-base method at 550 °C

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد20 (2) 2007

استخلاص ودراسة خواص طور الـ γ-ألومينا

رمزي رشيد علي العاني

قسم الكيمياء، كلية العلوم، الجامعة المستنصرية

الخلاصة

استعمل البوكسايت المستخرج من منطقة الكعرة-محافظة الأنبار الذي يحتوي على 55.08% وزناً أوكسيد الألمنيوم لإنتاج الألومينا الفعالة نوع كاما وباستخدام الطريقة الحامضية والطريقة الحامضية-القاعدية، شخصت الألومينا الناتجة بعد عملية الكلسنة باستخدام تقنية الأشعة السينية.

حضر عاملان مساعدان نوع بلاتين/ألومينا (0.35% بلاتين) باستخدام طريقة التحميل، وقد أسند أحد العاملين الى الألومينا المستخلصة ،والآخر على الألومينا المستوردة. وقد تم مقارنة فعالية العاملين المحضرين في تفاعلات التحول بوجود الهيدروجين للهبتان الاعتيادي وانتقائية العاملين المساعدين.

وقد أظهرت النتائج بأن العامل المساعد المسند الى الألومينا المستخلصة أكثر فعالية باتجاه تفاعلات تكوين نواتج الآيزومرة، في حين أن العامل المساعد المسند الى الألومينا المستوردة أكثر فعالية اتجاه تفاعلات تكوين المركبات الحلقية. وأظهرت النتائج أن العاملين المساعدين يسلكان السلوك نفسه تحت ظروف التفاعل المختلفة.