Modification of Mesopore Extrudate Gamma Alumina through Thermal Ammonia Treatment

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ABSTRACT: *A particular type of mesopore extrudates gamma alumina was prepared; which is used as the catalyst in the heavy oil desulfurization unit. Extrudates gamma alumina support has been made of the boehmite powder from Nephlinsinite mine ores (Surface Area (S.A.) >200* m^2/g*, Pore Volume (P.V.) =0.48* cm^3/g*, Average Pore Diameter (A.P.D.) = 8.10 nm); then, many samples of extrudate gamma alumina* (γ-Al_2O_3) *have been created to carry out a research the thermal and ammonia treatments under various operating situations (thermal effect 25,40,60,80 and 100ºC and Consecutive treatments) so as to exhibit the effects of different operating conditions on the pore volume and diameter in the prepared* γ-Al_2O_3 *heavy oil catalyst support. Textural properties of catalyst support have been identified by X-Ray Diffraction (XRD),* N_2*-adsorption/desorption, FT-IR, radial strength and Loss of Ignition (L.O.I) methods. The best effect of the ammonia treatment on the extrudate* γ-Al_2O_3 *support was observed after three ammonia treatments at 80ºC; under those circumstances, the resulted catalyst support has the highest amount of resemblance along with the commercial sample (S.A.=215.75* m^2/g*, P.V.=0.83* cm^3/g*, A.P.D. =15.49nm).*

KEYWORDS: *Thermal treatment; Gamma alumina* (γ-Al_2O_3)*; Mesoporous alumina, Desulfurization of heavy oil.*

INTRODUCTION

The Performance of a heterogeneous catalyst relies on its surface specifications such as surface area, pore volume, and pore diameter to a great extent. Since the main active parts of the catalysts are situated in their pores, the pore size distribution on the catalyst surface plays a role of controlling the activity of that catalyst; specifically, those reactions which require large molecules [1]. It is known that metals are advantageously deposited near the outside of catalyst pellets of extradites when catalyst is utilized with small pore. If catalyst with acceptably large pore is employed, it must be possible for those poisons to be dispersed more uniformly through the catalyst. This has to get rid of pore mouths plugging; accordingly it would expand the effective life of the catalyst [2].

Aluminum oxide (Al_2O_3), also known as alumina, has many stable transitional phases as gamma alumina (γ-Al_2O_3), delta alumina (δ-Al_2O_3), kappa alumina

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(κ-Al_2O_3), theta alumina (θ-Al_2O_3) and alpha alumina (α-Al_2O_3). Among these, γ-Al_2O_3 (activated alumina) has been widely utilized as catalyst, catalyst support, adsorbents and dehydrants due to its large particular surface area, good porosity, adsorbality and base characteristic [2, 3]. Several publications have stressed that γ-Al_2O_3 with high pore volume may become better the adsorption performance if used as an adsorbent, and loading capacity by using as a catalyst support to keep down diffusion and transport influences [4, 5]. For instance, in the petroleum industry γ-Al_2O_3 is usually applied as the catalyst support for hydrorefining which is the most significant approaches to become better the quality of oil products. This is especially important for Iran, where the crude oil is getting heavier and poorer in quality [5- 8].

Chemical approaches for producing γ-Al_2O_3 include sol-gel, hydrothermal, controlled precipitation of boehmite from either aluminum salts, alkoxides or metallic Powders. Several techniques such as the use of pore forming additives, controlling alumina precursor (e.g. boehmite) crystalline during precipitation and aging, thermal sintering, etc. have been released in literature for alumina support for catalysts with large pore volume and diameter [1- 3, 9,10]. *Park et al.* (2007) [11] tried the preparation of Al_2O_3 with an ionic liquid, a surface area of 470 m^2/g and pore volume of 1.46 cm^3/g. *Rinaldi et al.* (2005) [12] synthesized mesoporous γ-Al_2O_3 with relatively high surface area (325 m^2/g) and pore volume (2.08 cm^3/g) via the sol-gel method utilizing aluminum tri-sec-butoxide as the aluminum source. *Armor et al.* (1987) [13] reported the synthesis of high pore volume alumina (>5.00 cm^3/g) from aluminum isopropoxide by utilizing the supercritical solvent drying method. *Absi Halabi et al.* (1991) [14] explored the effect of the ammonia thermal treatment in an autoclave in the temperature range 150-300ºC on the preparing γ-Al_2O_3 support with large pore size distribution. *Vijayalakshimi et al.* (1998) [15] studied the surface modification of γ-Al_2O_3 by treatment with dilute NaOH and HCl and it is observed that micropores are demolished by the chemical treatment. *Liu et al.* (2015) [16] prepared aluminas by precipitating Al $(NO_3)_3.9H_2O$ with aqueous solution of ammonium carbonate. As a consequence, the alumina is calcined at 500ºC for 4 h under ambient atmosphere.

As mentioned above, boehmite powder with large pore is mostly produced by hydrolysis of aluminum alkoxide. Regarding the fact that the aluminum alkoxide is expensive and it is not available in our country Iran, therefore the finished price of the products by this method is notably high and it is not economical. Now concerning the existing background in this field, we can perceive advantage of this study which is to prepare γ-Al_2O_3 from the boehmite powder (as a precursor) extracted from Azarshahr Nephlinsinite mine ores. For the first time, catalyst support with large pore volume is prepared of the boehmite powder with ammonia treatment method. In this research, thermal ammonia treatment and the number of ammonia treatment have been studied comprehensively and the obtained results from this evaluation have been reported within this article. The boehmite powder has been made of the inexpensive materials with high accessibility to us regarding the existing background in this field, which seems to be a great advantage of this method of produced mesopore γ-Al_2O_3. Other than the mentioned treatments of the prepared mesopore γ-Al_2O_3 during this research finding, the crystalline properties of this product along with the optimization has been investigated during our research findings and our intended temperature. The execution of the aforementioned optimization process is lower than the same operating temperature in the similar optimization researches that their results have been reported in the formerly published articles.

EXPERIMENTAL SECTION

Materials

In this research, the boehmite powder which is extracted from Azarshahr Nephlinsinite mine ores, is applied as the precursor (S.A>200 m^2/g, P.V =0.48 cm^3/g, A.P.D.= 8.10 nm, 100mesh, XRD pattern of the boehmite sample are displayed in Fig.1 & Table 1 (Fig. 1 displays well defined observed XRD, and all peaks diffraction were completely indexed to the XRD pattern of pure bohemit (JCPDS card 01-083-2384). No XRD peaks demonstrating other crystalline phases were discovered, demonstrating that the boehmite powder revealed excellent crystallinity and a high purity.), the other raw materials; including ammonia (Merck, Germany), hydroxyethyl cellulose (Merck, Germany) are provided with a laboratory grade.

Table 1: The BET and BJH results of the effects of the concentration and treatment times.

Sample NO.	BET			BJH					
				Adsorption branch			Desorption branch		
	Surface Area (m^2/g)	Average Pore Diameter (nm)	Pore Volume (cm^3/g)	Pore Volume (cm^3/g)	Pore Radius (nm)	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Radius (nm)	Surface Area (m^2/g)
Commercial	231.72	12.60	0.72	0.72	6.03	246.19	0.78	3.10	385.89
untreated	239.88	9.06	0. 54	0. 54	4.04	261.90	0.594	3.01	387.24
S1	236.72	7.80	0.46	0.46	3.66	259.99	0.48	3.10	336.00
S2	213.33	10.72	0.57	0.57	6.03	241.78	0.45	4.62	194.15
S3	206.95	12.59	0.65	0.65	6.03	233.51	0.64	5.67	257.09
S4	208.05	12.64	0.65	0.65	4.62	241.37	0.67	4.04	286.73
S5	214.75	11.30	0.60	0.61	5.27	246.79	0.63	4.62	298.77
S6	208.05	12.64	0.65	0.65	4.62	241.37	0.67	4.04	286.73
S7	218.55	13.22	0.72	0.72	6.03	252.86	0.76	5.27	315.34
S8	215.75	15.49	0.83	0.83	7.94	230.09	0.83	5.27	266.45
S9	206.19	16.28	0.83	0.83	6.03	219.61	0.86	6.03	270.64

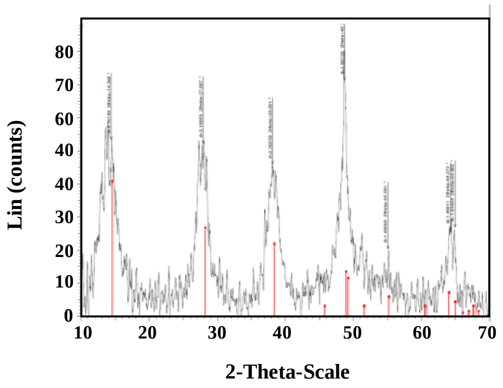

Fig. 1: XRD pattern of boehmite powder.

Characterization

The pore structure of the samples is measured by using N_2- adsorption/desorption porosimetry (Belsorp mini II, BEL JAPAN) according to ASTM: ISO 15901-2-2006 and ISO 15901-3-2007). All samples are degassed under vacuum at the temperature of 250ºC for 3 h before each measurement. The N_2-adsorption/ desorption isotherms are deployed to calculate the Brunauer–Emmett– Teller (BET) specific surface area. Pore volume and pore diameter distribution are computed by using the Barrett–Joyner–Halenda (BJH) method. The phase structure of the samples is studied by using X-ray diffraction (PW1800 model of PHILIPS devices) with a Cu Kα radiation source (λ = 1.54 Å), 2θ range from 20 to 90º at a scanning rate of 6 /min, step size=0.02, and operating at 40Ma and 40kV. L.O.I of extrudates were accomplished according to the ASTMD 7348-13 by with Heraeus furnace (Germany). FTIR was done by making KBr pellets (VERTEX 7 model of Brucker company, Germany).

Preparation method of untreated gamma alumina support

Boehmite powder is dried blended with 5% hydroxylethyl cellulose (HEC). Then acceptable distilled water is sprayed on it. The mixture is kneaded until a homogeneous paste is acquired. The paste is passed through the extruder and dried for two hours at the room temperature. It is kept in an oven at the temperature of 120 ºC for 24 h. Then, it is calcined up to 600 ºC for 6 h by using a furnace with temperature programing rate of 100 ºC/h to obtain the untreated catalyst support. The untreated catalyst support was possessed the following properties (length=2-7 mm, outer diameter=1.50mm, S.A=150-200 m^2/g, P.V<0.40 cm^3/g).

Temperature effect

The 5% ammonia solution is prepared in five separate containers. 10 g of prepared extrudate in previous section is added up to each container and is closed tightly the container and it was placed in the water bath that they are kept at 25, 40, 60, 80 and 100ºC for 8 h. Afterwards, its water was decanted and the extrudates are kept in an oven at 120 ºC for 24 h. The samples are named 1 to 5, respectively. For every treatment each sample was poured into container and samples are floated in 5% Ammonia solution.Thereupon, container`s holder is closed and bottle inserted into hot water bath at (80ºC) for one day.

The effect of the number of treatment times

The treated samples in 5% ammonia solution are retreated after calcination once more in the 5% ammonia solution (first treatment). The extrudates are held in a 120 ºC oven for 24 h (S6). At the same time, in other containers, samples are aged for the second time in 5% ammonia solution, the decanted solution and extrudates are kept at 120 ºC oven for 24 h (S7). Simultaneously, in other containers; samples are aged for the third time in 5% ammonia solution and extrudates are kept in a 120 °C oven for 24 h (S8). Retrospectively, samples are kept in separate containers for the fourth time in the ammonia solution. The extrudates are again put in the oven at 120ºC and then it is calcined up to 600 ºC for 6 h by using a furnace with temperature programing rate of 100 °C/h to obtain the untreated catalyst support.

RESULTS AND DISCUSSION

Textural properties

According to the IUPAC classification, all of the prepared mesopore γ-Al_2O_3 displayed type IV isotherms with H_2-type hysteresis loop, and representing typical mesoporous materials due to complex pore networks consisting of pores with wide pore size distribution. Figs. 2 and 3 reveal N_2 –adsorption/desorption isotherms for the thermal effect and number of ammonia treatment. As shown in Figs. 2, 3 and Table 1, thermal treatment and number of ammonia treatment do not significantly affect on the hysteresis loop shapes. Furthermore, all samples, commercial, untreated samples have the same hysteresis loop as type IV isotherms with H_2-type hysteresis loop.

Since the N_2–adsorption/desorption isotherm establish the relationship between the amount of N_2–adsorbed/desorbed gas and the pressure of adsorptive at the constant temperature, the same hysteresis loop as type IV isotherms shows that interaction between sample surface and adsorbate are relatively strong and the prosity of all samples is mesopore.

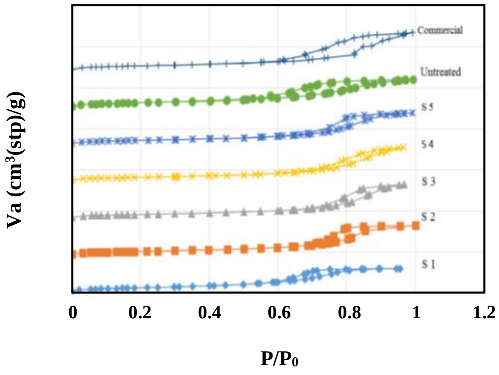

Fig. 2: Thermal effect on N_2-Adsorption/desorption isotherms.

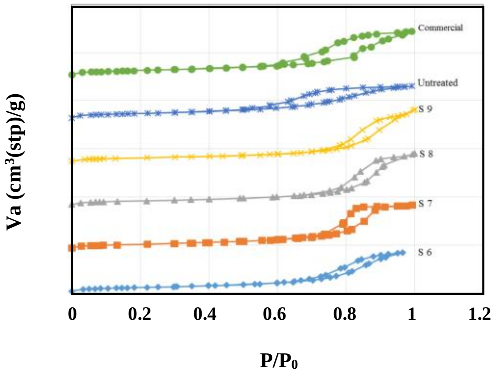

Fig. 3: Number of ammonia treatment effect on N_2- Adsorption/desorption isotherms

Thermal effect

As shown in Table 1, textural properties (specific surface area, pore volume and pore diameter) of S4 are the most similar to commercial sample.

In type IV adsorption isotherms, hysteresis occurs in the N_2–adsorption/desorption process. The hysteresis shape depends on the shape of mesopore materials. Whenever hysteresis exists, equilibrium adsorption/desorption is larger than that of at adsorption. This is mainly due to capillary condensation of N_2 gas in mesopore and there is diversity in meniscus between adsorption and desorption process.

As mentioned in the experimental section (thermal effect), the temperature of hydrothermal treatment was varied between 25 °C -100 °C because of its effect on pore size modification. Fig. 4 presents pore volume distribution data for heated samples at 25, 40, 60, 80 and 100 ºC. In the same way, the pore size distribution pattern is alerted; further enlargement of the pores with maximum pore volume in the S4 is the most similar to the commercial sample.

In order to compare the area distribution, y-axis is set to study on the dv_p/dr_P, and the Fig. 4 demonstrates that S4 has the most similarity to the commercial sample.

Table 1 displays the commercial sample ($r_{p,peak}$ (area) = 6.03nm), S4 ($r_{p,peak}$ (area) = 4.62 nm). Although the data of the BJH (saturated vapor pressure= 87.38kPa) plot for S4 and S3 are similar to the commercial sample, the BET data reveal that pore diameter and pore volume increase followed by the rise of temperature. Owing to the fact that sample at the 80ºC (S4) has the most significant influence on the properties of catalyst support, this temperature is selected as optimal temperature and all the next tests are carried out at 80º C as optimum temperature. Table 1 indicates the BET and BJH results of the N_2- adsorption/desorption porosimetry analysis. Figs. 2 and 4 show N_2-adsorption/ desorption methods, BJH plots of untreated, commercial, and S1-S5.

The results reveal that pores can be widened and pore size distribution in alumina support shifted from small pore size to the larger range by rising the temperature of treatment. Because of corrosive property of ammonia, it is inferred that pilling phenomena (A layer has been removed from the inner surface of pores) and destroyed amount of micropores has happened, which caused to expand the pore in diameter and volume.

Effect of the number of ammonia treatment

Ammonia is a base reactant, and it may strongly enhance the rate of hydroxylation of γ- Al_2O_3 by cleavage of the Al-O-Al bond. Such enhanced hydroxylation during the hydrothermal treatment may go up mobility of OH ions on alumina surface and rise up the rate of crystallization and particle agglomeration, then it results in pore enlargement.

As mentioned before, because of the capillary condensation of N_2 gas in mesopore, the shape of hysteresis loop in type IV adsorption isotherms are different. Therefore, in order to compare the area distribution, y-axis tends to investigate on the dv_p/dr_P, the Fig. 5 shows that the textural properties of S8 is most similar to the commercial sample [1]. As shown in Table 1 Textural properties (specific surface area, pore volume and average pore diameter) of S8 are the most similar to commercial sample.

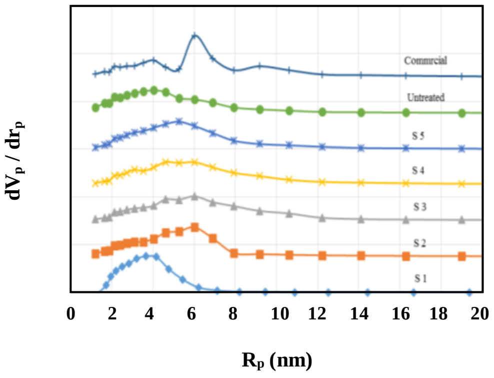

Fig. 4: Thermal effect on BJH plot (adsorbtion branch).

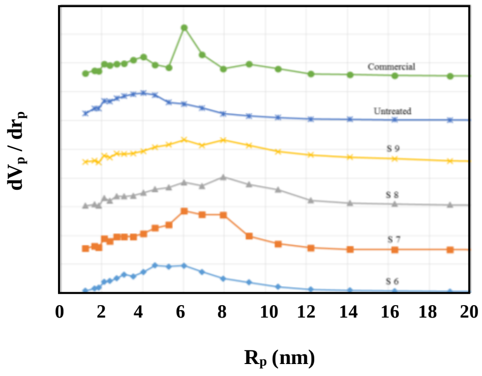

Fig. 5: Number of ammonia treatment effect on BJH plot (adsorbtion branch).

As shown in Table 1 and Fig. 5, the pore size of all treatment samples has up trend. By increasing ammonia treatment stage, the surface properties of the prepared catalyst support have improved, as far as the properties of S8 ($r_{p,peak}$ (area) = 7.94 nm) and S9 ($r_{p,peak}$ (area)= 6.03 nm) are better than commercial sample, because the S9 has lower radial strength compared with the commercial sample. Because of the S9 has low radial strength and easily crushed by slight hand pressure, thereupon; S8 is selected as the optimum prepared sample. According to the BJH plot, the pore volume and pore diameter of the S8 and S9 are close to the commercial sample. The BET plot data reveal that the properties of both samples

Table 2a: XRD data of the commercial, untreated, and optimized samples.

JCPDS Card no.004-0858	Commercial sample	Untreated sample	Optimized sample
	d-spacing (observed)	d-spacing (observed)	d-spacing (observed)
2.75	2.76	2.73	2.78
2.43	2.42	2.45	2.40
2.30	2.28	2.28	2.27
2.00	1.99	2.01	1.97
1.40	1.40	1.41	1.39

Table2b: XRD data of the Boehemite.

JCPDS Card no. 01-083-2384	Boehemite
	d-spacing (observed)
6.10	8.16
3.16	3.19
2.79	2.36
2.34	1.86
2.22	1.66

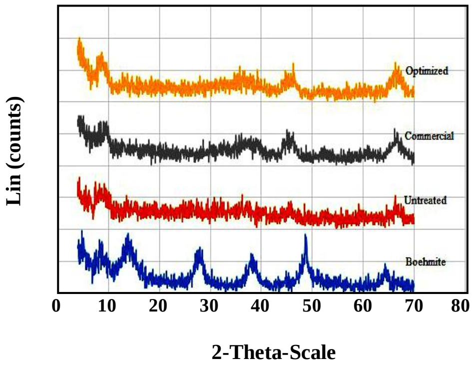

Fig. 6: XRD analysis spectra of the commercial), untreated, optimized and boehemit samples.

are better than the commercial ones, but S8 has the stronger mechanical strength and bigger surface area.

XRD analysis

As shown in Table 2 (a,b) & Fig. 6, crystalline structure of the commercial sample, untreated sample, and optimum prepared sample (S8) are characterized by using XRD technique. All results were in acceptable agreement with the simulated XRD Pattern of γ-alumia (JCPDS no. 004-0858). The boehemite specific peak was appeared in 14° (2θ) and the specific peak of the untreated sample was appeared in 65° (2θ) which was clearly visible in all samples expect boehemite. Accordingly, it could be concluded that the number of ammonia treatment and thermal treatment do not affect on the crystalline phase and support character [17]. Therefore, these results confirmed by FT-IR results.

FT-IR Results

FT-IR analysis has been used as a useful technique to investigate the difference between boehemite and γ- Al_2O_3. In Fig. 7, the FT-IR spectra of boehemite (AlO (OH)) normally show a broad band in the spectral range of (3200 – 3600) cm^{-1} which is dedicated to –OH stretching vibration due to hydrogen bonding formation of this group in Al_2O_3. In this region the peak, are related to the amount of –OH group, because of the number of H2O molecules and consequently hydrogen bond generation. In this region (3200 – 3600) cm^{-1}, the weak peak appear for γ- Al_2O_3s, which is due to decreasing in number of molecule. The peak at~ 1600 cm^{-1} is assigned to the bending mode of water molecules in the boehmite and in γ-Al_2O_3 structure too which is assigned to –OH bending vibrational mode. The vibrational mode for both boehmite and γ- Al_2O_3 are similar [18]. The FTIR spectra of boehmite at ~ 1100 cm^{-1} show a peak which is assigned to Al-OH bond. Condensation of AlO (OH)

Table 3: Results of the radial strength measurment of commercial, untreated and all samples.

Sample name	Radial strength (N/mm)
Commercial sample	6.75
Untreated sample	6.90
S1	6.88
S2	6.80
S3	6.70
S4	6.00
S5	5.50
S6	6.70
S7	6.65
S8	6.50
S9	5.80

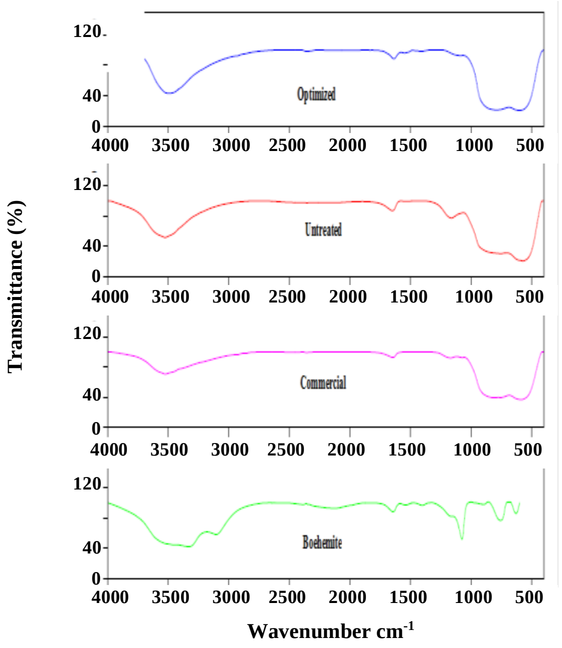

Fig. 7: FT-IR analysis spectra of the commercial), untreated, optimized and boehemit samples.

into Al-O-Al can also be in other reason for the removal of adsorbed water molecules from boehmite phase and formation of γ-Al_2O_3. The appearance of moderately weak peaks at~ 600 cm^{-1} are assigned to Al-O stretching mode of AlO_6. The two small peaks in the range of ~ (600-800) cm^{-1} are stressed on converting the phase of the samples from boehmite structure to γ-Al_2O_3.

Radial strength analysis

Radial strength measurment is done according to ASTMD 4179-11 standard. Table 3 shows the results of radial strength.

The goal of this research is to achieve mesopore extrudates γ-Al_2O_3 compared with commercial sample properties. The results of thermal effect display that S4 and S5 have the better textural properties. The S5 has lower mechanical strength than S4, as a result S4 is selected as the best sample to study the effect of the number of treatments. The results of treatments number present that the S8 and S9 have the better textural properties. Because of S9 radial strength is less than commercial sample, S8 is selected as the optimum sample.

Loss on Ignition (L.O.I)

In this method lose of mass determination in air at 900ºC and 1 h shows up humidity or lose of impurity (unphase transferred). According to the ASTMD 7348-13 dried sample weighted by analytical balance and kept in furnace for 1 h was at 900ºC. Then, it transferred to desicator until cooled and at the end it weighted again. The difference between the fist and final weight was calculated.

Less L.O.I. defines amount of impurity and less moisture absorption of catalyst which is observed maximum loss in S8 and S9 samples. The amount of humidity adsorption would go up in accordance with increasing of pore volume and pore diameter. As a result, this analysis is significant (Table 4).

Table 4:L.O.I. analysis results of the commercial, untreated and all samples.

Sample name	Loss on Ignition (LOI) (%)
Commercial	15.48
Untreated	13.33
S1	13.34
S2	13.35
S3	13.48
S4	14.27
S5	14.38
S6	14.27
S7	14.53
S8	14.72
S9	15.23

CONCLUSIONS

Finally, it has been concluded that thermal treatment and number of ammonia treatment times highly affect on the pore volume and average pore diameter of the extrudate mesopore γ-Al_2O_3, and the important effective parameters with their reasons have been discussed based on the resulted facts and figures from the aforementioned laboratory test reports.

- The purpose of this research leads to achieve a catalyst support with large mesopore size by domestic and inexpensive materials at the mild conditions. For this reason, both the temperature and concentration are low.
- The optimum thermal operating condition to prepare mesopore extrudate γ-Al_2O_3 with desired pore volume and pore diameter was at 80°C.
- The three times ammonia treatments have been selected as optimum ammonia treatment numbers to prepare mesoporore extrudate γ-Al_2O_3 with desired pore volume and pore diameter and radial strength.
- According to these results, sample properties were improved by increasing the number of ammonia treatment and increasing the temperature of treatment. But increasing the number of ammonia treatment plays an important role than the thermal treatment.
- As a very important result of this study, the optimum operating conditions in the ammonia treatment have been selected for the preparation of mesopore extrudate γ-Al_2O_3 with proper physical and chemical properties used as a catalyst support in the heavy oil desulfurization unit.
- The applied catalyst support in heavy oil desulfurization (commercial sample) should possess the following properties (S.A=170-250 m^2/g, P.V=0.7 ± 0.05 cm^3/g, A.P.D=12 ± 0.50 nm). The properties of S8 as an optimum sample (S.A=215 m^2/g, A.P.D=15.49 nm, P.V=0.83 cm^3/g) are closed to the commercial sample in most cases and even more desirable in some.

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