# Improvement of Heavy Oil Hydrodesulfurization Catalyst Support Properties by Acetic Acid Treatment

***Shahidian, Zahra; Zare, Karim****[+]

*Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, I.R. IRAN*

**ABSTRACT:** *A specific type of mesopore extrudates gamma alumina was prepared; which is applied as the catalyst in the heavy oil hydrodesulfurization unit. Extrudates gamma alumina has been devised the boehmite powder; several samples have been utilized to investigate the concentration and the number of acetic acid treatment effects on the textural properties. Textural properties of catalyst support have been characterized by X-Ray Diffraction, $N_2$-adsorption/desorption techniques, the best results were observed at 25% acetic acid after three times treatments. The active metals (3.71%Molybdenium &1.43%Nickle) have been impregnated on the catalyst support. The prepared catalyst determined by X-Ray Fluorescence, $N_2$- adsorption/desorption, bench scale reactor test, $NH_3$-Temperature Programmed Desorption and Radial Strength techniques.*

**KEYWORDS:** *Acidic treatment; Gamma alumina ($\gamma$-$Al_2O_3$); Mesopore support; Heavy oil hydrodesulfurization catalyst.*

## INTRODUCTION

Alumina has been largely employed as a significant industrial material in the fields of catalyst support, catalyst, ceramic, adsorbent and membrane because of its specific physical and chemical qualities [1-3]. Since it displayed different crystal phases with a wide range of surface areas, alumina is fairly stable involving acidic and basic sites [3-5]. Gamma alumina applied in the petroleum refining industry as catalyst support. For reactions containing large, the large pore size of the alumina support plays an important role in affecting the activity of the catalyst. Therefore, wide pore gamma alumina catalysts have also been realized to be more effective in heavy oil hydrodesulfurization [6-10].

Recently, research on the preparation of gamma alumina supports with wide pores has been invigorated by the upgrading of heavy oil cuts by controlling gamma alumina catalyst support. Several methods such as the use of pore forming agents, controlling alumina precursor (e.g. boehmite), the usage of poring agents crystalline during precipitation treatment, and thermal sintering has been described in literature for creating alumina support at catalysts with wide pore volume [11-14].

*Aguado A. et al.* (2010) has analyzed the influence of the high thermal treatment over the textural properties of sol-gel mesoporous $\gamma$-$Al_2O_3$ synthesized in acid medium using cationic surfactants as templates [15]. *Choi J, et al.* (2017) prepared mesoporous $\gamma$-$Al_2O_3$ particles by the usage of a boehmite slurry which was prepared through thermal acid treatment of commercial boehmite with various concentrations of $HNO_3$ [16]. *Stanislaus A, et al.* (2001)

* *To whom correspondence should be addressed.*
*+ E-mail: k-zare@sbu.ac.ir*
*1021-9986/2020/3/71-80 10/$/6.00*

has investigated the changes occurring in the alumina phase during hydrothermal treatment of γ -alumina in the presence and absence of agents such as P, F, phenol and acetic acid. As a part of the study, a large pore Ni-Mo/γ-$Al_2O_3$was prepared by hydrothermal treatment procedure.The catalyst showed a remarkably high activity for hydrodemetallization and asphaltenes conversion reactions in vacuum residue hydroprocessing [7]. *Absi-Halabi et al.* (1993) investigated the influence of acidic and basic vapors on pore enlargement of y-alumina supports under high temperature hydrothermal conditions (from 150 to 300°C) [17].

In the first section of this article, the specific properties of $\gamma$-$Al_2O_3$ are introduced. Based on the mentioned specific properties; mesoporous $\gamma$-$Al_2O_3$ is known as a very suitable catalyst support in many catalytic applications and because of those characteristics $\gamma$-$Al_2O_3$ has a wide range of applications, then it has the required flexibility to provide us with different pore volumes and diameters. Ni-Mo/$\gamma$-$Al_2O_3$ can benefit from the catalyst in the heavy oil hydrodesulfurization unit which require to have large pore volume and large pore diameter so as to be considered as Ni-Mo/$\gamma$-$Al_2O_3$, as a result it can be used as the catalyst in the heavy

Oil hydrodesulfurization unit.

In the second part, the required materials and different methods are set to cover up by preparing extrudates γ-$Al_2O_3$ and Ni-Mo/$\gamma$-$Al_2O_3$. The physical and chemical properties of the untreated sample, all treated and commercial samples have been analyzed; thus those properties have been compared with the same ones of commercial sample by utilizing different analysis laboratory apparatuses such as X-Ray Diffraction (XRD), $N_2$- adsorption/desorption, and radial strength [18,19]. In the third section, the results have been reported acquired from testing different samples using $N_2$-adsorption/desorption experiment, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), $NH_3$-Temperature Programmed Desorption ($NH_3$-TPD) and bench scale reactor test by comparing different results with each other and commercial sample.

## EXPERIMENTAL SECTION

### *Materials*

In this research, the boehmite powder which is extracted from Azarshahr Nephlinsinite mine ores, used as the precursor (S.A>200 $m^2$/g, P.V =0.48 $cm^3$/g, A.P.D.= 8.10 nm, 100mesh) and the other raw materials; including acetic acid (Merck, Germany), hydroxyethyl cellulose (Merck, Germany), ammonium hepta molybdate tetra hydrate, nitric acid, and Nickel (II) nitrate, hexahydrate were provided regarding laboratory grade.

### *Characterization*

The pore structure of the samples is measured by using $N_2$-adsorption/desorption porosimetry (Belsorp mini II, BEL JAPAN). All samples are degassed under vacuum at the temperature of 250ºC for 3 h before each measurement (Belprep vac II, BEL JAPAN), this analysis was done in liquid Nitrogen at 77K. The $N_2$-adsorption/ desorption isotherms are applied 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) technique. The phase structure of the samples is checked by using X-Ray Diffraction (PW1800 model of PHILIPS devices) with a Cu Ka radiation source (l = 1.54 Å) and a 2$\theta$ range from 20 to 90º at a scanning rate of 6 /min. X-Ray Fluorescence (XRF) analysis is carried out with the PW1480model of PHILIPS device. The bench scale reactor test is accomplished under the special feed condition. It can be conducted a study with $NH_3$-TPD analysis by using Micromeritics ChemiSorb 2750 apparatus.

### *Preparation method of heavy oil hydrodesulfurization catalyst and catalyst support*

*The general method for preparing extrudates gamma-alumina support*

Boehmite powder was blended with 5% hydroxylethyl cellulose (HEC). Then adequate water was sprayed on it. The mixture was kneaded until a homogeneous paste was obtained. The paste was passed through the extruder and dried for two hours at the room temperature. It was kept in an oven at 120 ºC by a day, then it was calcined up to 600 ºC by using a furnace with temperature programing rate of 100 ºC/h to obtain the untreated catalyst support, and the gamma alumina phase is formed at the boehmite powder in this section. 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<0.54 $cm^3$/g), A. P. D = 9.10 nm.

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

| Sample NO. | BET | | | BJH (Adsorption branch) | | | BJH (Desorption branch) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Average Pore Diameter (nm) | Surface Area ($m^2/g$) | 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 ($m^2/g$) |
| Untreated | 9.06 | 239.88 | 0.54 | 0.54 | 4.04 | 261.90 | 0.59 | 3.10 | 387.24 |
| Sample 1 | 16.57 | 163.41 | 0.67 | 0.67 | 2.73 | 177.91 | 0.68 | 3.10 | 188.73 |
| Sample 2 | 10.27 | 256.19 | 0.65 | 0.65 | 4.62 | 290.24 | 0.69 | 3.54 | 355.07 |
| Sample 3 | 9.85 | 245.81 | 0.60 | 0.60 | 4.62 | 281.15 | 0.63 | 3.54 | 341.79 |
| Sample 4 | 16.57 | 163.41 | 0.67 | 0.67 | 2.73 | 177.91 | 0.68 | 3.11 | 188.73 |
| Sample 5 | 14.32 | 254.21 | 0.91 | 0.90 | 5.45 | 247.96 | 0.89 | 4.04 | 363.90 |
| Sample 6 | 17.38 | 234.59 | 0.90 | 0.89 | 6.23 | 219.09 | 0.92 | 6.03 | 338.24 |
| Sample 7 | 17.27 | 215.11 | 0.92 | 0.92 | 8.19 | 199.30 | 0.95 | 6.03 | 285.65 |
| Commercial | 16.88 | 186.19 | 0.78 | 0.78 | 7.94 | 194.12 | 0.82 | 5.27 | 269.55 |
| Prepared | 17.059 | 208.52 | 0.88 | 0.88 | 7.94 | 226.00 | 0.91 | 5.27 | 275.46 |

*Concentration effect*

Three acetic acid solutions of 25% (Sample 1), 50% (Sample 2), and 99% (Sample 3) were prepared because of evaluating the influence of acetic acid concentration. 15 g of the extruded catalyst support were added to each container in closed containers; then, the extrudates were kept in these solutions for 5 days. Afterwards, decanted solution and extrudes were placed in an oven at 120 ˚C during the night. They were calcined up to 600 ˚C in a furnace with the heating rate of 100 ˚C/h until acetic acid completely removed. Table 1 shows the BET and BJH results of the $N_2$-adsorption/desorption porosimetry analysis. Fig. 1-a, 4-a and 5-a (in appendix) show $N_2$-adsorption/ desorption methods, BJH plots of untreated, and three samples. S1 is chosen as the selected concentration.

*The effect of the number of acetic acid treatment times*

The treated samples in 25% acetic acid (Sample 4) solution were treated after calcination once more in the 25% acetic acid solution (first treatment), in the second treatment the extrudes were kept in a 120 ˚C oven by a day (Sample 5). At the same time, in other containers, samples were aged for the third time in 25% acetic acid solution, the decanted solution and extrudes were kept in a 120 ˚C oven for a day or night (Sample 6). At the same time, in other containers, samples were aged for the fourth time in 25% acetic acid solution and extrudes were retained in a 120 ˚C oven by a day (Sample 7). All samples are calcined after final treatment. Table 1 shows the BET and BJH results of $N_2$-adsorption/desorption porosimetry analysis. Fig. 2-a, 8-a & 9-a display $N_2$-adsorption/desorption, and BJH plots of untreated, and the four samples.

***Preparing heavy oil hydrodesulfurization catalyst***

About 94.86 g of optimal catalyst support was made to prepare 100 g of the heavy oil hydrodesulfurization catalyst. Then, 4.55 g of ammonium hepta molybdate tetra hydrate was dissolved in 132.36 ml of denionized water and pH was stabilized with nitric acid at 4. 5.96 g dried Nickel (II) nitrate hexa hydrate was added into the solution. The optimal catalyst support were added to the solution. In order to impregnate the active metals, the solution was placed in the thermal cabinet with thermal programed and was heated from room temperature to 120 °C. Afterwards, because of stabilizing the active metals to form oxide metals, the catalyst calcined in furnace with thermal programed at 600 ˚C for 6 h. Table 1 displays the BET and BJH results of $N_2$-adsorption/desorption porosimetry analysis. Fig. 3-a, 6-a and 7-a show $N_2$-adsorption/desorption, BJH plots of prepared and commercial heavy oil hydodesulfurization catalyst.

## RESULTS AND DISCUSSION

***Textural properties***

According to the IUPAC classification, all of the prepared mesopore $\gamma$-$Al_2O_3$ and Ni-Mo/$\gamma$-$Al_2O_3$ exhibited

type IV isotherms with $H_2$ hysteresis loop. Representing typical mesoporous materials due to complex pore networks consist of pores with wide pore size distribution. Fig. 1-a, 2-a & 3-a represent $N_2$–adsorption/desorption isotherms for the concentration effect, number of acetic acid treatment, and heavy oil hydrodesulfurizaion catalyst. As shown in Fig. 1-a, 2-a, 3-a and Table 1, acetic acid concentration and number of acetic acid treatment do not significantly affect on the hysteresis loop shapes, all samples, untreated samples, prepared and commercial heavy oil hydrodesulfuriztion catalyst. They have the same hysteresis loop as type IV isotherms with $H_2$ hysteresis loop.

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

***Concentration effect***

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

In type IV adsorption isotherms, hysteresis occurs in the $N_2$ –adsorption/desorption process. The hysteresis shape depends on the shape of mesopore. Whenever hysteresis exists, equilibrium adsorption/desorption is larger than the one at adsorption. It is mainly due to capillary condensation of $N_2$ gas happens in mesopore and there is different in meniscus between in adsorption process and in desorption method. In order to compare the area distribution, y-axis is set to investigate on $dv_p/dr_P$.According to the Table 1 and Fig. 4-a, Sample 1 properties are most similar to the commercial ones.

***Effect of the number of acetic acid treatment***

As mentioned before, the shape of hysteresis loop in type IV adsorption isotherms is different because of the capillary condensation of $N_2$ gas in mesopore. As a result, in order to compare the area distribution, y-axis is set to study on $dv_p/dr_P$. The Fig. 8-a indicates that Sample6 is most similar to the commercial one.

As shown in Table 1 textural properties (specific surface area, pore volume and pore diameter) of Sample 6 are the most similar to commercial one. Table 1 and Fig. 8-a determine that Sample 6 is most closely resembled to commercial one.

Samples cannot be treated over than three times because their mechanical strength become less than commercial sample, then they would lose their mechanical strength. In Table 1, It can be observed that the sample properties improve in each treatment process, the best properties are obtained by the third treatment.

***XRD analysis***

As shown in Table 2 and Fig. 10, crystalline structure of the commercial sample, untreated sample, and optimum prepared sample (Sample 6) are characterized by using XRD. According to the XRD results, the d-spacing in the untreated, commercial, and optimum prepared samples match with peaks for $\gamma$-$Al_2O_3$ crystalline structure; hence, they all possess a $\gamma$-$Al_2O_3$ crystalline structure, accordingly acetic acid treatment do not affect on the crystalline structure.

***XRF***

XRF analysis is done on the prepared heavy oil hydrodesulfurization catalyst and the results are compared with commercial one. The XRF results are summarized in Table 3.

***Radial strength analysis***

Radial strength analysis is carried out according to ASTM D4179-11. In addition, Table 4 indicates the results of radial strength.

As mentioned before, among samples with desirable surface area, models with suitable appearance radial strength (Sample6) were selected as the example for the radial strength analysis.

***$NH_3$-TPD analysis***

In a typical analysis, 0.25 g of the sample was degassed at 500 °C under a helium flow rate of 30 mL/min for 60 min at a heating rate of 10°C/min. Then, the sample was cool down at 150 °C and saturated with a mixture of helium and 2 vol.% ammonia (2 vol.% $NH_3$/He) for 40 min. Next, the sample was purged with a helium flow for 30 min to remove weakly and physically

***Table 2: XRD pattern of untreated, and optimized catalyst support 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 |

***Table 3: XRF pattern of commercial and prepared heavy oil hydrodesulfurization catalyst.***

| | Commercial heavy oil hydrodesulfrization catalyst | Prepared heavy oil hydrodesulfurization catalyst |
|---|---|---|
| NiO (wt%) | 1.43 | 1.20 |
| $MoO_3$ (wt%) | 3.71 | 3.85 |

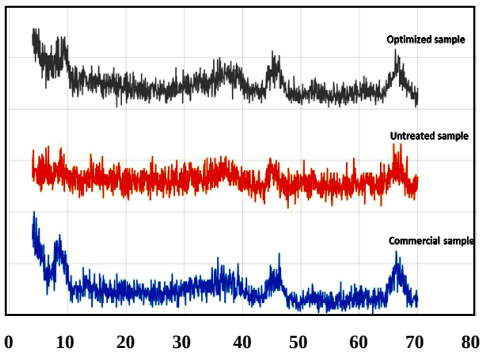


***Fig. 10: XRD analysis spectrum of the commercial (a), untreated (b) and optimized (c) samples***

adsorbed $NH_3$ on the surface of the catalyst. Afterwards, the sample was cooled off at 90 °C, then it heated at a rate of 10 °C/min under a flow of helium carrier gas (40 mL/min) from 90 °C to 700 °C. Eventually, the amount of ammonia effluent was measured using TCD and recorded as a function of temperature.

$NH_3$-TPD profile for Ni-Mo/$\gamma$-$Al_2O_3$ catalyst is shown in Fig. 11. With this catalyst (Sample6), the desorptgram demonstrated two well resolved peaks with middle and high temperature ones at 420 ˚C and 880 °C. These results indicated that two types of adsorption sites for $NH_3$-TPD were present on the catalyst. The high temperature peak consisted of $N_2$ and $H_2$ gases from the decomposition of $NH_3$. The middle temperature peak was due to release of $NH_3$ adsorbed from alumina and introduced the strong acidic sites.

***Bench scale reactor test***

The investigated catalyst (sample6) in this research is Ni-Mo/$\gamma$-$Al_2O_3$ which is applied in fixed bed reactors. It has these following features: vertical stainless steel, 1200 mm in height, 20 mm diameter, is equipped by furnace with 975 mm length and GC Mass detector. Light gas oil as feed is employed in fixed bed reactors in heavy oil hydrodesulfurization units with the following specifications: (Table 5), (LGO, S: 1.20 wt. %); vacuum gas oil (VGO, S: 2.64 wt. %, CCR: 0.08 wt. %) and vacuum gas oil containing heavy oil (VGO.AR, S: 2.68 wt. %, CCR: 0.54 wt. %, Ni: 0.50 ppm, V: 1.90 ppm). Table 6 exhibits the results of the bench scale reactor test.

## CONCLUSIONS

Taking the advantage of this research is to prepare $\gamma$-$Al_2O_3$ from the boehmite powder (as a precursor) extracted from Azarshahr Nephlinsinite mine ores. For the first time, catalyst support with large pore volume is put together of the boehmite powder through acetic acid treatment method. In this study, the mesopore $\gamma$-$Al_2O_3$ optimization and acetic acid treatment have been researched completely and the obtained results from this assessment have been reported within this article.

Consequently, it has been concluded that acetic acid treatment affect on the pore volume and surface area

***Table 4: Radial strength analysis results of untreated catalyst support, commercial, and prepared heavy oil hydrodesulfurization catalyst.***

| | Untreated catalyst support | Commercial catalyst | Prepared catalyst |
|---|---|---|---|
| Radial Strength (N/mm) | 14.60 | 13.89 | 13.70 |

***Table 5: The feed specifications for catalyst bench scale reactor test.***

| | |
|---|---|
| Feed S | 1.11 wt% |
| Ni-V | 53.00 ppm |
| P | 60bar |
| T | 400K |
| LHSV | $0.50 m^3/m^3.h$ |
| $H_2$/Oil | 1000 mol/mol |

***Table 6: The results of the bench scale reactor test.***

| Heavy Oil Desulfurization Catalyst | Prepared Catalyst | Commercial Catalyst |
|---|---|---|
| Sulfur conversion% | 80.90 | 69.00 |
| Sulfur conversion after catalyst deactivation% | 47.70 | 30.00 |
| Nickel and Vanadium conversion% | 86.70 | 87.00 |
| Nickel and Vanadium conversion after catalyst deactivation% | 54.70 | 54.10 |

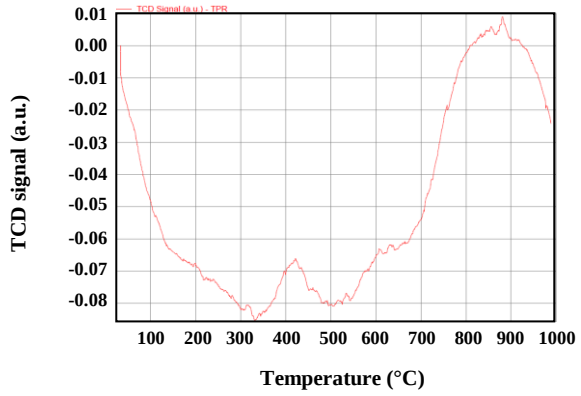


***Fig. 11: $NH_3$-TPD analysis spectrum of the prepared sample.***

of the extrudates mesopore heavy oil hydrodesulfurization catalyst, besides the important affecting parameters along with their reasons have been discussed based on the resulted facts and figures from the aforementioned laboratory test reports.

- As a very important result of this discussion, the optimum operating conditions in the acetic acid treatment have been chosen for the preparing a mesopore extrudates Ni-Mo/$\gamma$-$Al_2O_3$ with proper physical and chemical properties to be applied as a catalyst in the heavy oil desulfurization unit.
- Acetic acid 25% has been picked out as optimum acetic acid concentration to equip mesopore extrudates $\gamma$-$Al_2O_3$ with desired pore volume and surface area.
- The three times acetic acid treatment have been selected as optimum acetic acid treatment numbers to prepare mesopore extrudates $\gamma$-$Al_2O_3$ with desired pore volume and surface area and radial strength.
- According to the results, sample properties were improved by increasing the number of acetic acid treatment. Neither different acetic acid concentration treatment nor the number of aging and impregnation active metals do not influence on the crystalline phase and support character. However, operating treatment and impregnation active metals were modified the textural properties. All treatments and impregnation active metals did not impact on the mesopore extrudates $\gamma$-$Al_2O_3$ structure. As a result of treatment, all mesopore for $\gamma$-$Al_2O_3$ were wider than before treatment. Furthermore, impregnation active metals, pore volume and pore diameter were smaller than before impregnation.

● The applied catalyst in atmospheric residual crude oil hydrodesulfurization (commercial sample) should possess the following properties (S.A=170-250 $m^2/g$, P.V=0.70±0.05 $cm^3/g$, A. P.D=12±0.5 nm). The properties of prepared heavy oil hydrodesulfurization catalyst (S.A=227 $m^2/g$, A. P.D=14.27 nm, P.V=0.83 $cm^3/g$) are similar to the commercial sample in most cases and even more desirable in some cases.

Under those circumstances, it would be possible to prepare heavy oil hydrodesulfurization catalyst with desired and favorable pore volume, surface area and the percentage of Sulfur, Nickel and Vanadium conversions in the commercial scale; moreover it can be scaled up to be set up in the industrial scale.

*Received : Sep. 9, 2018 ; Accepted :Jan. 28, 2019*

**REFERENCES**

[1] Ancheyta J., "Catalyst, Deactivation of Heavy Oil Hydroprocessing Catalyst", John Wiley & Sons, Inc., Hoboken, New Jersey, (2016).

[2] Rashidzadeh M., Peyrovi M.H., Mondegarian R., Alumina-Based Supports for Automotive Palladium Catalysts, *React. Kinet. Catal. Lett.*, **69**: 115-122 (2000).

[3] Absi-Halabi M., Stanislaus A., Al-Zaid H., Studies on Pore Size Control of Alumina: Preparation of Alumina Catalyst Extrudates with Large Unimodal Pore Structure by Low Temperature Hydrothermal Treatment, *Preparation of Catalysts V*, **63**: 155-163 (1991).

[4] Rinaldi R., Schuchardt U., On the Paradox of Transition Metal-Free Alumina-Catalyzed Epoxidation with Aqueous Hydrogen Peroxide, *J. Catal*, **236**: 335-345 (2005).

[5] Park H., Yang S. H., Jun Y. S., Hong W. H., Kang J. K., Facile Route to Synthesize Large-Mesoporous γ-Alumina by Room Temperature Ionic Liquids, *Chem. Mater*., **19**: 535-542 (2007).

[6] Rayo P., Ancheyta J., Ramírez J., Alejandre A.G., Hydrotreating of Diluted Maya Crude with NiMo/$Al_2O_3$-$TiO_2$ Catalysts: Effect of Diluent Composition, *Catalysis Today*, **98**: 171-178 (2004).

[7] Stanislaus A., Al-Dolama K., Absi-Halabi M., Preparation of a Large Pore Alumina-Based HDM Catalyst by Hydrothermal Treatment and Studies on Pore Enlargement Mechanism, *Journal of Molecular Catalysis A: Chemical*, **181**: 33-39 (2002).

[8] Peyrovi M.H., Hamoule T., Study of Catalytic Properties of Pt/Al-HMS Catalysts in *n*-heptane Hydroisomerization, *Kinet. Mech. Cat.*, **106**: 233-243 (2012).

[9] Speight J.G., "Introduction of Handbook of Refinery Desulfurization", Handbook of Refinery Desulfurization, CD & W, Inc. Laramie, Wyoming, (2016).

[10] Kabe T., Aoyama Y., Ishihara D. Wang, A., Qian W.H, Hosoya M, Effects of $H_2S$ on hydrodesulfurization of Dibenzothiophene and 4,6-Dimethyldibenzothiophene on Alumina-Supported NiMo and NiW Catalysts, *Q. Appl. Catal. A*, **209**: 237-247 (2001).

[11] Liu Y., Jia L., Hou B., Li D., Preparation and Characterization of Transitional Alumina Obtained Through Ammonia Treatment, *Bulletin of the Korean Chemical Society*, **36**: 2851-2861 (2015).

[12] Armor J. N., Carlson E. J., Variables in the Synthesis of Unusually High Pore Volume Aluminas, *J. Mater. Sci*., **22**: 2549-2556(1987).

[13] Li Z. T., Liu D. M., Cai Y. D., Yao Y. B., Wang H., Pore Structure and Compressibility of Coal Matrix with Elevated Temperatures by Mercury Intrusion Porosimetry, *Energy Explor. Exploit*, **33**: 809-826 (2015).

[14] Parida K. M., Pradhan A. C., Sahu J. Das, N., Synthesis and Characterization of Nano-Sized Porous Gamma-Alumina by Control Precipitation method, *Mater. Chem. Phys*., **113**: 244-248 (2009).

[15] Aguado J. A., Escola J. M., Influence of the Thermal Treatment upon the Textural Properties of Sol–Gel Mesoporous γ-Alumina Synthesized with Cationic Surfactants, *Microporous and Mesoporous Materials*, **128**: 48-55 (2010).

[16] Choi J., Yoo K.S., Kim S.D., Park H.K., Nam C.W., Kim J., Synthesis of Mesoporous Spherical γ-Al2O3 Particles with Varying Porosity by Spray Pyrolysis of Commercial Boehmite, *Journal of Industrial and Engineering Chemistry*, **56:** 151-156 (2017).

17] Absi-Halabi M., Stanislaus A., Al-Zaid H., Effect of Acidic and Basic Vapors on Pore Size Distribution of Alumina under Hydrothermal Conditions, *Applied Catalysis A: General*, **101**: 117-128 (1993).

[[18] Xu J., Ibrahim A.R., Hong Y., Su Y., Wang H., Li J., Preparation of Large Pore Volume γ-Alumina and Its Performance as Catalyst Support in Phenol Hydroxylation, *Microporous and Mesoporous Materials*, **231**: 1-10 (2016).

[19] www.iesmat.com/ Physical Adsorption Characterization of Mesoporous Materials: Comments on Hysteresis, part1.

## Appendix

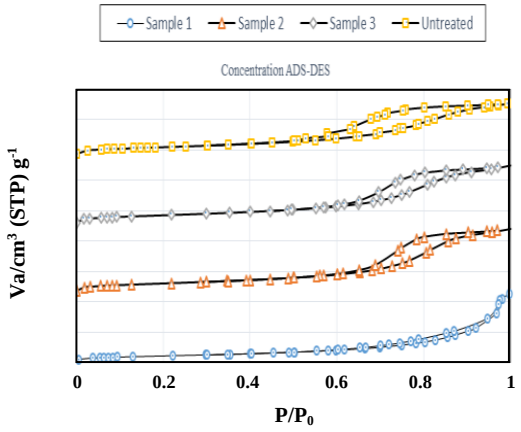


***Fig. 1a: Acetic acid concentration effect on $N_2$-Adsorption/ desorption isotherms.***

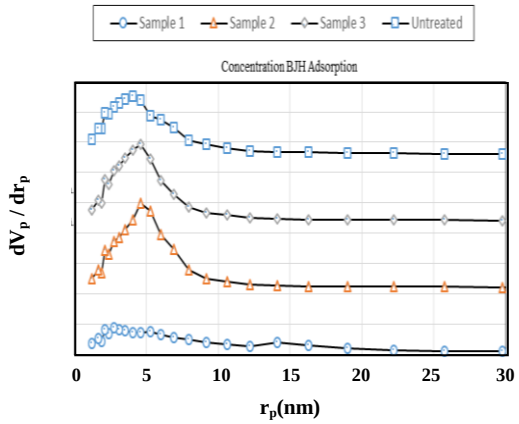


***Fig. 4a: Acetic acid concentration effect on BJH plot adsorption branch***

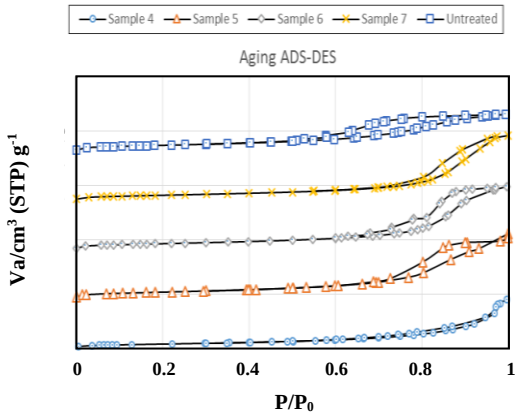


***Fig. 2a: Number of acetic acid treatment effect on $N_2$-Adsorption/desorption isotherms.***

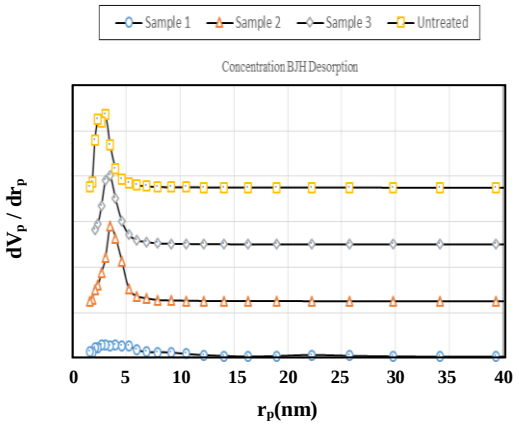


***Fig. 5a: Acetic acid concentration effect on BJH plot desorption branch.***

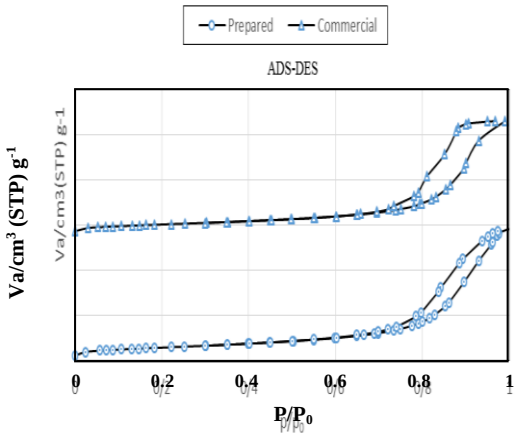


***Fig. 3a: $N_2$-Adsorption/desorption isotherms prepared and commercial heavy oil desulfurization catalyst***

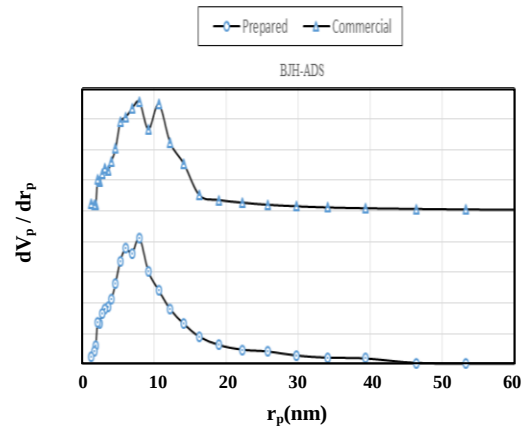


***Fig. 6a: Adsorption branch of the BJH plot of the heavy oil desulfurization catalyst.***

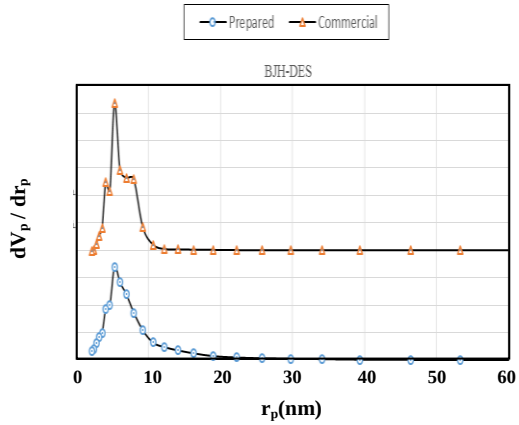


***Fig. 7a: Desorption branch of the BJH plot of the heavy oil desulfurization catalyst.***

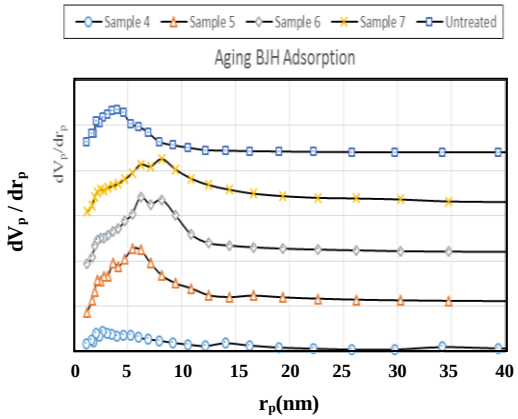


***Fig. 8a: Number of acetic acid treatment effect on BJH plot adsorption branch.***

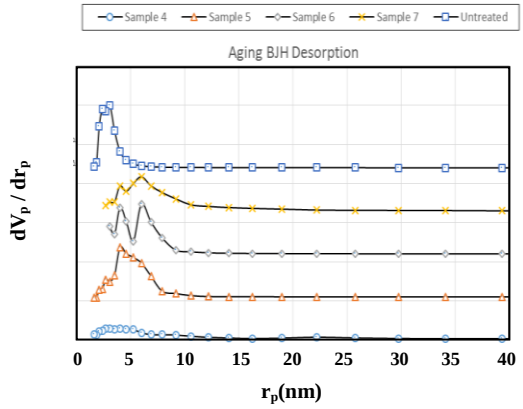


***Fig. 9a: Number of acetic acid treatment effect on BJH plot desorption branch.***