Bull. Chem. Soc. Ethiop. **2025**, 39(3), 473-482. ISSN 1011-3924
© 2025 Chemical Society of Ethiopia and The Authors Printed in Ethiopia
DOI: https://dx.doi.org/10.4314/bcse.v39i3.7 Online ISSN 1726-801X

PREPARATION AND CHARACTERIZATION OF A MIXED CATALYST OF COBALT AND MOLYBDENUM CARRIED ON ALUMINUM OXIDE PREPARED FROM BENTONITE ORE

Qaidar Salim Jarjees[1], Aws Nazar Abdlaziz[1], Abbas Rafaa Qasim[2*] and Ammar Ahmed Hamdoon[1]

[1]Department of Chemistry, College of Education for Pure Science, University of Mosul, Mosul, Iraq
[2]Nineveh Education Direstorate, Ministry of Education, Mosul, Iraq

(Received October 9, 2024; Revised November 12, 2024; Accepted November 12, 2024)

ABSTRACT. The research aims to select one of the natural ores (bentonite clays) for preparing alumina (Al_2O_3) and using it as a support material for the catalyst. The components of the ore were studied using modern techniques such as energy dispersive X-ray (EDX) technique and X-ray fluorescence (XRF) technique. Then, alumina (aluminum oxide) was prepared from the bentonite ore after a series of chemical treatments were carried out on it in order to remove the components that negatively affect the effectiveness of the catalyst under study. After that, the catalyst consisting of transition elements (cobalt/molybdenum) supported on alumina was prepared and its chemical content was identified and the weight and atomic percentages were determined by measuring energy dispersive X-rays (EDX) and identifying its thermal stability by conducting thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The structure of the prepared catalyst was examined using BET technique and SEM (scanning electron microscope) measurement, in addition to X-ray diffraction (XRD) and X-ray fluorescence (XRF) measurements to identify the percentages of the minerals composing the catalyst, and then estimate the percentage of these elements in their oxide form.

KEYWORDS: Catalyst, Bentonite, Cobalt, Molybdenum

INTRODUCTION

Due to the many uses of catalysts and their importance in the field of industry, oil refining and petrochemical industries, and as a result of their high prices that reach hundreds of thousands of dollars, which increases the cost of production, and since most industrial catalysts have a direct impact on the environment in terms of pollution with heavy metals or gases resulting from refining or industry, natural ores that are available in good quantities in various regions of Iraq have been exploited, including bentonite clay as a raw material for preparing the catalyst.

Bentonite clay is a natural ore with several uses, and has received great attention in the industrial field because it is balanced in terms of structural, mechanical and adsorption properties. Bentonite clay belongs to a group of smectic minerals, which are characterized by their ability to swell and expand when in contact with water. This unique property of smectic clay such as bentonite gives it the ability to be very effective in various industrial and commercial fields. The complex crystal structure of bentonite, evident in the arrangement of alumina and silica layers, gives the element exceptional swelling properties and ion exchange capacity [1].

Bentonite ore consists mainly of montmorillonite, with other components such as beidellite, saponite and many other minerals. Bentonite has structures consisting of a single aluminum plate and an octahedral (O) molecule located between two silicate plates with some of the silicate tetrahedral atoms replaced by aluminum atoms or octahedral atoms (Al^{+3} or Mg^{+2}), there are two types of bentonite: sodium bentonite and calcium bentonite [2] .

---

*Corresponding authors. E-mail: abbas.21esp12@student.uomosul.edu.iq

Clay minerals are a diverse group of hydrated aluminosilicates that exist in the form of layers or polymeric structures. Clay minerals have received great attention in recent years due to their many properties, such as natural abundance, high reactivity, and low cost [3].

Alumina (aluminum oxide) is one of the most widely used materials in industry due to its high modulus of elasticity, resistance to chemical corrosion, stability and strength retention at high temperatures. Pure alumina exists in two basic forms, alpha-alumina and gamma-alumina, and is found in the form of beta-alumina, but it is impure. Alpha-alumina (corundum) is the most stable form in physical properties, as it melts at a temperature of 1700-1800 °C and its density is high [4].

The most important industrial process for alumina is its use in the field of adsorption, and it has been shown through many studies that it can be used as an adsorbent for heavy metals and dyes from sewage water. Due to its high surface area and stability at wide temperatures, it is used as a catalyst for most chemical reactions [5].

Cobalt-molybdenum (Co-Mo) alloys and their composites are important catalysts in industry because they have good stability and high corrosion resistance which results from the electronic configuration between them, as the crystal structure is more stable when Mo is added to the structure of Co element, and then a remarkable effect can be achieved by alloying the (d) electron shell of both cobalt and molybdenum, which is the main source of catalytic activity, corrosion resistance and mechanical strength. The d-orbital contains electrons that participate in chemical reactions, increasing the reaction rate by forming partial covalent bonds. This aids in stabilizing the reactive state and prevents the disintegration of unstable compounds. It also helps to provide an ideal electronic balance that enhances corrosion resistance, making the resulting materials more effective in challenging environments. It should be noted that the catalytic activity generally arises from the high free energy present on the semi-stable surface, as cobalt-molybdenum alloys with different surface shape can be prepared from aqueous systems containing Co(II) and Mo(VI) [6].

Aim of the research

This research aims to use one of the natural clays (bentonite) which is found in large quantities in Qarah Tapah area in Diyala Governorate as a primary source for preparing aluminum oxide (alumina) used as a support material for a mixed catalyst consisting of cobalt and molybdenum (Co-Mo/Al_2O_3) and to identify the properties of the catalyst and know its components and the extent of its effectiveness and the possibility of benefiting from it in the future in the catalytic treatment of petroleum derivatives.

EXPERIMENTAL

Preparation of the clay ore

Bentonite ore was selected for its high content of silica and aluminum using the conventional geological method followed by the General Company for Geological Survey in Baghdad from the upper layer to the lower layer, as the ore is found in the form of irregular sediments or rocks in the Qarah Tapah area in Diyala Governorate.

Preparation of the sample for study

A specific weight of the natural ore (bentonite) was taken and ground with a hand mortar and then sieved using a 200-mesh sieve. A quantity of ethanol was added to it, The addition of ethanol improves the grinding process by reducing heat, decreasing material clumping, evenly breaking down raw particles, and facilitating the extraction of the desired compounds from bentonite ore while the grinding process was carried out continuously to reduce the effect of the crystalline structures of the minerals in the sample by the heat generated during the grinding process. After that, the ore was dried for 6 hours [7].

Analysis of bentonite ore

The chemical analysis of the bentonite ore was carried out using the EDX technique in order to identify the type of elements present in it and determine their percentage in their oxide form.

Steps to prepare the ore

Removal of carbonates from natural ore

150 g of the ore was taken after preparing it in the previous steps and placed in a round-bottom flask with a capacity of 500 mL, and 300 mL of a 10% hydrochloric acid (HCl) solution was added to it. Thermal sublimation was carried out using a reflux condenser in a round-bottom flask for 3 hours, and it was cooled to the laboratory temperature, and the solution was filtered and the precipitate was washed with distilled water several times and dried at a temperature of 125 °C for 5 hours in an electric oven, then it was placed in the desiccator and after the weight stabilizes, it is weighed, as the difference in weight represents the amount of carbonates removed from the natural ore [8,9].

Iron removal from clay ore

The treated clay ore in the previous paragraph was taken, and placed in a round-bottom flask with a capacity of 500 mL and 200 mL of a solution of 4% sodium dithionite ($Na_2S_2O_4$) was added to it, and the thermal sublimation process was carried out with a reflux condenser for two hours and cooled at laboratory temperature, the solution was filtered, and the precipitate was taken and washed with distilled water and treated with 200 mL of hydrochloric acid (10%) in a round-bottom flask with a capacity of 500 mL, and the thermal sublimation was carried out for an hour and the flask was cooled to laboratory temperature, then the precipitate was filtered and washed with distilled water, then it was dried in an electric oven at a temperature of 120 °C for 3 hours, then it was transferred to a beaker with a capacity of 500 mL, and 100 mL of the toluene was added to it with continuous shaking and heating to a temperature of 70 °C for 30 min. After that, it was filtered and dried at a temperature of 120 °C for two hours. After the weight stabilizes, it is weighed, as the difference in weight represents the amount of iron removed from the mineral ore [10].

$$\mathrm{Na_2S_2O_4} + \mathrm{Fe} \rightarrow \mathrm{FeS}\downarrow + \mathrm{S} + 2\mathrm{NaOH}$$

$$\mathrm{FeS} + 2\mathrm{HCl} \rightarrow \mathrm{FeCl_2} + \mathrm{H_2S}$$

Non-crystalline silica removal from clay metal raw

The sample of the treated ore in the previous two paragraphs was taken, and placed in a round-bottom flask with a capacity of 500 mL and 250 mL of sodium hydroxide solution (0.5 M) was added to it, it was thermally sublimated with a reflux condenser for 5 hours, then the flask was left to cool at laboratory temperature, then the remaining mineral ore was filtered and washed with distilled water, then dried at a temperature of 120 °C for 3 hours and transferred to the desiccator. After the precipitate stabilizes, the weight is taken, and the decrease in weight represents the amount of non-crystalline silica that was converted to sodium silicate [11, 12].

Preparation of aluminum oxide (alumina) from the ore

The sample of the treated mineral ore in the previous paragraphs was taken after removing the carbonates, iron and non-crystalline silica and placed in a beaker with a capacity of (500 mL) and (100 mL) of distilled water was added to it with heating and continuous shaking using a mechanical device at a temperature of (70 °C), then (100 mL) of concentrated sulfuric acid was added to it drop by drop until the acid was finished, then it was placed in a (500 mL) flask and thermal sublimation was carried out with a reflux condenser for one hour, then the solution was left to cool at the laboratory temperature and then filtered using ashless filter paper No. (24) with washing with distilled water several times, then the filtrate was taken and a few drops of phenolphthalein indicator were added to it and adjusted by adding ammonium hydroxide solution (25%) drop by drop with continuous stirring until the indicator color became light pink, then the mixture was heated to boiling point for 10 min, then left to settle for 15 min and filtered using ashless filter paper No. (24) and left to dry at the laboratory temperature for 24 hours, then the precipitate was placed in an electric oven at a temperature of 120 °C for a period of 5 hours, then it was transferred with the filter paper to a ceramic bowl, and the burning process was completed in an electric furnace at a temperature of 600 °C for two hours, after which the sample representing aluminum oxide (gamma-alumina) was weighed [13-15].

$$\mathrm{Al_2O_3.3H_2O + H_2SO_4 + 8H_2O \rightarrow Al_2(SO_4)_3.14H_2O}$$
$$\mathrm{Al_2(SO_4)_3.14H_2O + NH_4OH \rightarrow AlO(OH)\downarrow + (NH_4)_2SO_4}$$
$$\mathrm{AlO(OH) \overset{\Delta}{\rightarrow} Al_2O_3}$$

Preparation of cobalt and molybdenum catalyst carried on alumina

10 g of the previously prepared Gamma-Alumina (Alumina) were taken and placed in a ceramic bowl and heated to (250 °C) for (one hour), then (3.6 g) of cobalt nitrate was weighed in a (250 mL) beaker and (10 mL) of distilled water was added to it to dissolve it. Then it was placed in a separating funnel to add it drop by drop to the alumina, where the solution was placed after the addition in an electric oven for drying at (120 °C) for one hour, then after that the addition process was repeated in the same way and the same amount of cobalt nitrate was taken for the purpose of performing the sequential impregnation process, after which (5 g) of $(NH_4)_6Mo_7O_{24}.4H_2O$ was weighed and dissolved in (250 mL) of distilled water and heated to (50 °C) for three hours, where it was added to the previous (alumina) solution with continuous shaking for (3 hours), then the solution was left for (12 hours) to soak, after which it was placed in a bowl in an electric oven for drying for (6 hours) at (120 °C), then it was placed in a calcining furnace at (550 °C) for (2 hours) [16] .

RESULTS AND DISCUSSION

A study and analysis of bentonite ore was conducted using energy dispersive X-Ray (EDX) technique to determine the percentage of elements present in it. It was found that the ore is mainly composed of silica (35.24%) and aluminum (18.5%), as well as the ore containing different percentages of iron, calcium and potassium, some of which will be removed by treatment, as shown in Table 1. The content of the ore of carbonates and bicarbonates was also identified, which are present in the form of natural non-clay minerals such as calcite ($CaCO_3$) or dolomite [$Ca,Mg(CO_3)_2$] or appear in the form of non-metallic carbonates such as silica (in its crystalline and non-crystalline types). The presence of carbonates has a negative effect on the quality of the prepared catalysts due to their interference during their preparation, so it is preferable to remove them before the catalyst preparation process. The same measurement was carried out for the prepared catalyst and it was found that there were peaks for each of (cobalt/molybdenum), which is evidence of the process of supporting the minerals on alumina, as well as a decrease in the percentage of silica. We also note the increase in the percentage of aluminum in the catalyst as in Figure 1.

Table 1. The chemical analysis of bentonite ore as weight percentages of elements in the form of oxides.

Oxides	Bentonite Wt. (%)
SiO_2 (crystal)	35.24
SiO_2 (amorphous)	22.2
Al_2O_3	18.5
Fe_2O_3	3.7
CaO	6.2
MgO	5.4
Na_2O	0.17
K_2O	0.27
Loss in ignition	13.6

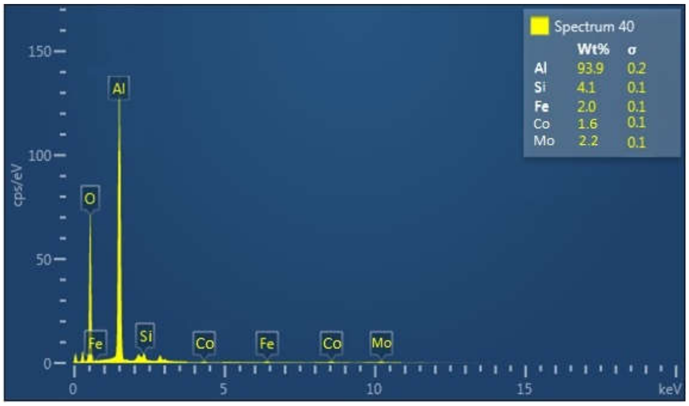


Figure 1. EDX for prepared catalyst (Co-Mo).

As for thermogravimetric analysis (TGA) of the prepared catalyst to determine the amount and type of water molecules present in it, the clay ores lose the water molecules adsorbed on the surface at a temperature of (110 °C), while the water molecules present inside the channels of the porous crystal structure are lost at a temperature higher than (250 °C). When the temperature is raised to higher than (350 °C), we notice the loss of hydroxyl groups present in the composition of the ores in the form of water molecules [17, 18], as each two hydroxyl groups turn into a water molecule leaving one oxygen atom on the crystal structure of the ore, while the calcination of carbons begins by losing CO_2 gas and converting its elements into an oxide form after a temperature of (500 °C) and up to a temperature of approximately (700 °C). Figures 2 and 3 show the measurement of TGA and differential analysis respectively for the prepared catalyst.

The XRD measurement of the prepared catalyst was performed to determine its content of clay and non-clay minerals, in addition to identifying the crystalline patterns specific to each mineral and comparing them with the standard diffraction patterns (AMCSD, 2023). Figure 4 shows the XRD measurement of the prepared catalyst, where we notice a match with the standard sample of alumina by comparing the diffraction patterns and the values of the atomic distances (d-spacing) and the angles (2θ) that belong to aluminum oxides (boehmite and gibbsite), the measurements of the catalyst showed that it consists of quartz (SiO_2) at 2θ (26.34-42.47) and a small amount of calcite, which is the crystalline form of $CaCO_3$, this was removed from the raw material during the purification process. Hematite (Fe_2O_3) is present at 2θ (24.15-33.95) and was previously removed using sodium dithionite, as its presence could affect the catalyst's efficiency and performance, in addition to the appearance of multiple bands belonging to cobalt and molybdenum that appear clearly in the band (40.62) as shown in Table 2.

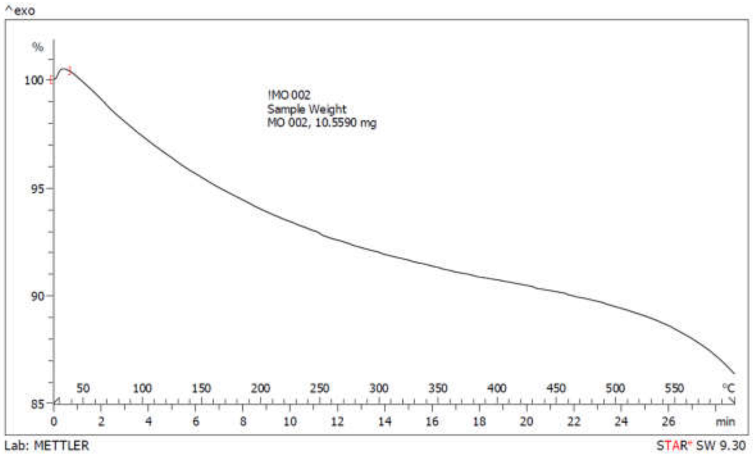


Figure 2. TGA curves for prepared catalyst (Co-Mo).

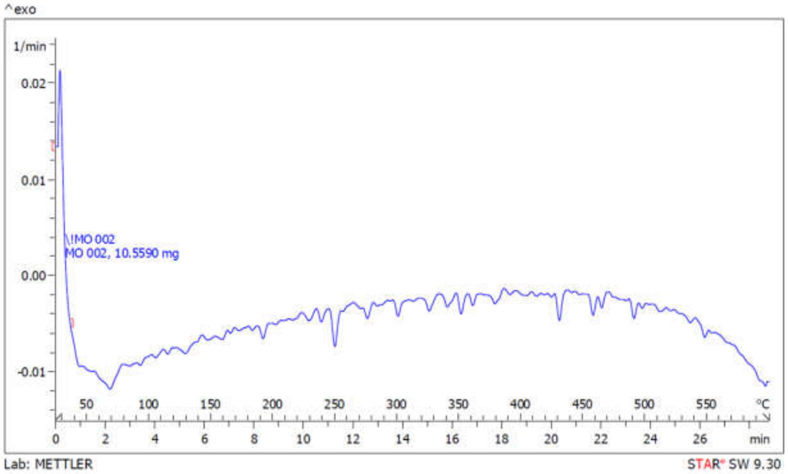


Figure 3. DTA curves for prepared catalyst (Co-Mo).

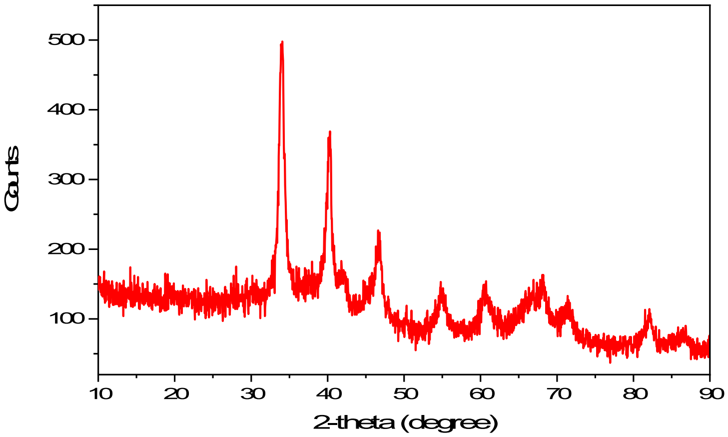


Figure 4. XRD for catalyst (Co-Mo).

Table 2. XRD analysis for prepared catalyst (Co-Mo).

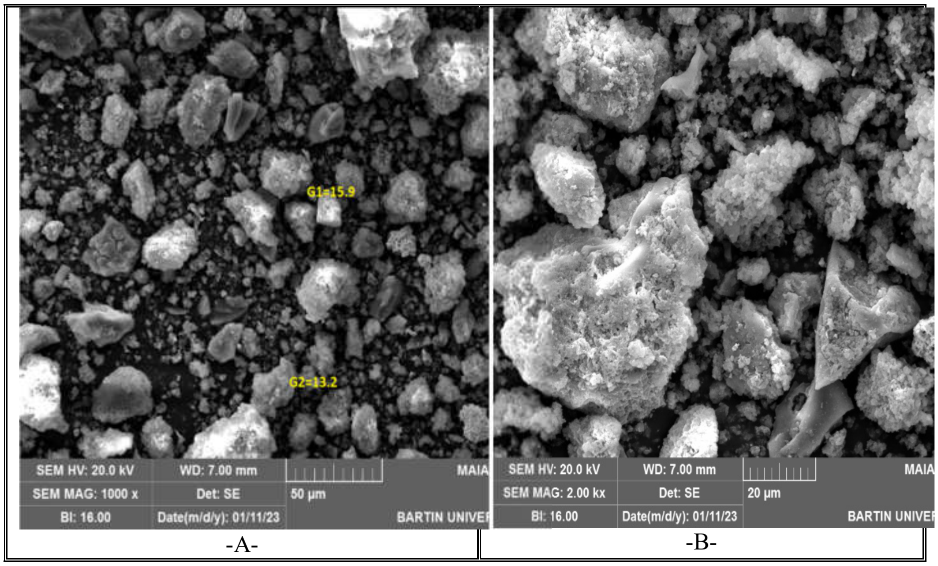
Minerals	2θ	d-spacing	Crystallite size (nm)
Boehmite $AlO(OH)$	9.901 45.39 71.80	0.1355 1.9855 1.3147	1.033 0.0756 0.1280
Gibbsite $Al(OH)_3$	20.68 46.69	4.3573 1.9336	0.0323 0.0772
Cobalt	44.26 51.57	2.0462 1.7721	0.0731 0.0863
Molybdenum	40.62 58.80	2.2210 1.5705	0.0664 0.1001
Quartz SiO_2	26.35 42.47	3.3446 2.1287	0.0425 0.0697
Hematite Fe_2O_3	24.15 33.95	3.6855 2.7028	0.0384 0.0536

As for the X-ray fluorescence (XRF) technique for both the bentonite ore and the prepared catalyst, an analysis was conducted for them in the laboratory of the Northern Cement Plant in Iraq, and it was found that there was a clear change in the proportions of the elements at varying rates as shown in Table 3, where we note that the bentonite ore consists mainly of aluminum and silicon, while for the prepared catalyst, we note a significant decrease in the proportion of silica, carbonates and iron, indicating that an actual removal process has occurred, with the presence of low proportions of cobalt and molybdenum in the oxide form, and this proves that the process of supporting has actually occurred on the alumina.

Regarding the results of the (FE-SEM) image by scanning electron microscope of the catalyst under study, it was found that the catalyst grains are more regular in one area and another area has a crystalline shape with different sizes. It was also found that the catalyst nano-sizes appeared ranging between (9.9-15.9) nanometers, which indicates that the process of supporting the catalyst on the alumina increased the appearance of the nano-sizes of the grains as shown in Figure 5.

Table 3. XRF analysis for bentonite and prepared catalyst (Co-Mo).

Metal oxides	Percentage ratio (%) of bentonite	Percentage ratio (%) of catalyst
Al_2O_3	44.68	67.88
SiO_2	24.7	10.217
Fe_2O_3	6.772	4.679
CaO	3.342	1.356
CuO	0.0422	0.0258
ZnO	0.0060	0.0028
CoO	--------	7.752
MoO_2	--------	3.145
V_2O_5	0.355	0.344
TiO_2	4.962	0.076
Nb_2O_5	0.0753	0.002
Yb_2O_3	0.028	0.003
SrO	0.0215	0.0115
K_2O	0.133	0.1672
Re_2O_7	0.004	------
IrO_2	0.0047	------



-A- -B-

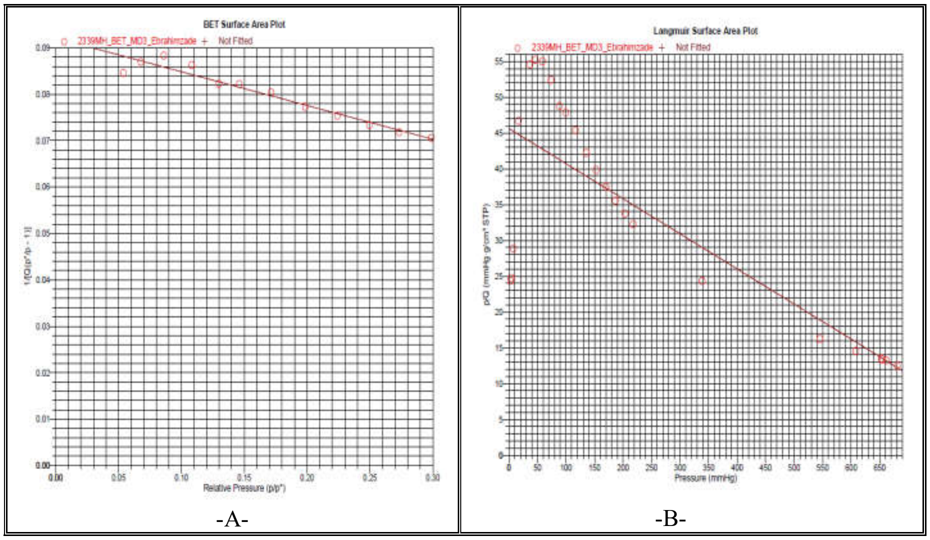
Figure 5. SEM for prepared catalyst (Co-Mo).

When conducting BET analysis of the prepared catalyst, which is one of the methods used in physical chemistry and through which the surface area of the metals is known, the surface area of the catalyst under study was measured and showed excellent data, as the surface area reached (224.0000 m²/g) and was measured by the Langmuir method, as it reached (-88.8410 m²/g). The Langmuir surface area is a method used to estimate the effective surface area of a material based on the principle of adsorption on the surface. This model is particularly useful in cases where surfaces have specific and limited adsorption sites, such as certain porous materials or catalysts. This high area gives a greater ability to adsorption and increases the effectiveness. The size and diameter of the pores were also measured, as shown in Table 4 and Figure 6.

Table 4. BET analysis.

Measurements	Analysis data
BET surface area	224.0000 m²/g
Langmuir surface area	-88.8410 m²/g
Pore volume	0.073510 cm³/g
Pore size	1.31267 nm

Pore volume is the measurement of the amount of voids or empty spaces within a material, which can be filled with air or liquids. It is usually expressed in milliliters per gram or cubic meters per kilogram. Pore volume plays a significant role in the material's ability to absorb gases or liquids. While pore size is the measurement of the overall diameter or the diameter of the voids within the material. It is usually expressed in nanometers or micrometers. One type of pore is the micropore, which has a diameter of less than 2 nanometers. When examining the measurement of the prepared catalyst, we notice that it has excellent pores (1.31267 nm), which is less than 2 nanometers.



-A- -B-

Figure 6. A surface area by BET method, B surface area by Langmuir method.

CONCLUSION

It was shown through the measurements and the results of the prepared catalyst Co-Mo/Al_2O_3 that it has a clear crystalline shape, a high surface area, diverse porous channels, and good thermal stability, in addition to benefiting from the natural mineral ore used as a low-cost and environmentally friendly raw material in preparing the support material (alumina), and when comparing with a previous study [19] that used bauxite clay instead of bentonite to prepare alumina (supporting), it was found that the surface area of the catalyst had increased compared to the previous one. It was also shown that the properties of the Co-Mo/Al_2O_3 catalyst have a stronger reactive nature than Ni-Mo/Al_2O_3. There is a study that will be published later showing the catalytic ability of the catalyst in the field of catalytic reforming of petroleum derivative (kerosene).

ACKNOWLEDGEMENTS

We would like to acknowledge college of Education for Pure Science, Mosul University for the support they provided to complete this research.

REFERENCES

1. Bangar, S.P.; Ilyas, R.A.; Chowdhury, A.; Navaf, M.; Sunooj, K.V.; Siroha, A.K. Bentonite clay as a nanofiller for food packaging applications. *Trends Food Sci. Technol.* **2023**, 142, 104242.
2. Ibrahim, A.S.; Al-Bidry, M.A. Study the effect of particle sizes and concentration on the rheological properties of Iraqi bentonite for using as drilling fluids. *J. Eng.* **2020**, 26, 65-76.
3. Wang, S.; Gainey, L.; Mackinnon, I.D.; Allen, C.; Gu, Y.; Xi, Y. Thermal behaviors of clay minerals as key components and additives for fired brick properties: A review. *J. Build. Eng.* **2023**, 66, 105802.
4. Khadhir, S.A.; Abed, M.A.; Ahmed, O.A. Study of alumina compounds prepared via two different hydrogen functions by co-precipitation method. *J. Educ. Sci.* **2022**, 5, 42.
5. Mohammed, M.K.; Fahmi, A.H.; Mourad, S.H. Removal of sulfur compounds from Iraqi crude oil using γ-Al2O3 nanoparticles. *Bull. Chem. Soc. Ethiop.* **2024**, 38, 1241-1250.
6. He, X.; Hu, Z.; Yang, J.; Guo, R.; Wu, L. Co-deposition of nanocrystalline Co–Mo catalysts with a new fluffy microstructure for hydrogen evolution reaction based on N,N-dimethylformamide and ethylene glycol system. *Int. J. Hydrogen Energy* **2023**, 48, 31506-31518.
7. Pansu, M.; Gautheyrou, J. *Handbook of Soil Analysis, Mineralogical, Organic and Inorganic Methods.* Springer-Verlag, Berlin; **2006**; pp. 15-18, 226-233.
8. Adekola, F.A.; Olosho, A.I.; Baba, A.A; Adebayo, S.A. Dissolution kinetics studies of nigerian gypsum ore in hydrochloric acid. *J. Chem. Technol. Metall.* **2018**, 53, 845-855.
9. Loeppert, R.H; Suarez, D. *Carbonate and Gypsum*, Publication from USDA – ARS/UNL/ Faculty, University of Nebraska, Lincoln; **1996**; p. 504.
10. Papassiopi, N.; Vaxevanidou, K.; Paspaliaris, I. Effectiveness of iron reducing bacteria for the removal of iron from bauxite ores. *Miner. Eng.* **2010**, 23, 25-31.
11. Boricha, A.B.; Bajaj, H.C.; Jasra, R.V.; Ghosh, P.; Ghosh, P.K. Process for the recovery of palladium from spent silca. *U.S. Patent* **2006**, 7, 108, 839.
12. Nibori, Y.; Kunita, M.; Tochiyama, O.; Chida, T. Dissolution rates of amorphous silica in highly alkaline solution. *J. Nucl. Med. Technol.* **2000**, 37, 349-357.
13. Al-Dabbagh, S.M. Alum Production from Local Bauxite Ores, Proceedings of the Continuing Education Course, University of Mosul, Iraq; **2008**; p. 145.
14. Ali, A.H.; AL-Taie, M.H.; Ayoob, I.F. The extraction of alumina from kaolin. *Eng. Technol.* **2019**, 37, 133-139.
15. Gougazeh, M. Removal of iron and titanium contaminants from Jordanian Kaolin's by using chemical leaching. *J. Taibah Univ. Med. Sci.* **2018**, 12, 247-254.
16. Hussein, S.J.; Aoyed, K.K.; Ibrahim, S.K.; Mehawee, I.K. Synthesis and characterization of Co-Mo/γ-alumina catalyst from local kaolin clay for hydrodesulfurization of Iraqi naphtha. *J. Pet. Sci. Res.* **2021**, 30, 84-106.
17. Michael, E.B. *Introduction to Thermal Analysis*, 2nd ed., Kluwer Academic Publisher; London; **2004**; pp. 19-28.
18. Bevis, J.; Bottom, R.; Duncan, J.; Farhat, I.; Forrest, M.; Furniss, D.;Seddon, A. *Principles and Applications of Thermal Analysis*, Wiley Online Library; **2008**; pp. 88-97.
19. Jarjees, Q.S.; Qasim, A.R.; Hamdoon, A.A. Synthesis and characterization of nickel and molybdenum catalysts supported on alumina derived from bauxite. *Bull. Chem. Soc. Ethiop.* **2024**, 38, 1715-1724.