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SYNTHESIS AND CHARACTERIZATION OF NICKEL AND MOLYBDENUM CATALYSTS SUPPORTED ON ALUMINA DERIVED FROM BAUXITE

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ABSTRACT. In this study, a natural ore (bauxite), which is characterized by its high content of various aluminum minerals, such as gypsite, $Al(OH)_3$, bohmite, and diaspore, AlO(OH), was used to obtain alumina (Al_2O_3), which was used as a support for the catalyst. The components of the ore were studied using multiple techniques, such as The X-ray energy dispersion (EDX) technique, X-ray diffraction (XRD) and X-ray fluorescence (XRF) technology. Then, undesirable components that negatively affect the behavior of the prepared catalyst were removed, such as carbonates, iron, and amorphous silica, and then aluminum oxide (alumina) was prepared from the ore using a series of chemical treatments. Then the mixed catalyst consisting of (nickel/molybdenum) carried on alumina was prepared, its properties were studied, and its components were identified by measuring energy dispersion with X-rays (EDX) and ensuring the extent of its thermal stability by conducting a thermal analysis measurement. Gravimetric analysis (TGA), differential thermal analysis (DTA), measurement of the surface area of the prepared catalyst (BET), scanning electron microscope (SEM) measurement, as well as X-ray diffraction (XRD) and X-ray fluorescence (XRF) measurements to identify the percentages of metals, and then estimating the percentage of these elements in their oxide form.

KEY WORDS: Catalyst, Bauxite, Nickel, Molybdenum

INTRODUCTION

The Earth's crust contains many clay minerals and ores, which are used in many industrial applications. Bauxite is the most commonly used natural ore to produce aluminum metal, and it is the most widely used element in chemical industries. The aluminum industry is constantly rising with the increase in population and industries, so in 2021 Australia was the largest bauxite-producing country in the world, estimated at about (110) million tons, followed by China, Brazil, India, and others. The Bayer process is one of the best biological methods for industrial uses in the process of refining aluminum from bauxite ore [1].

Clay minerals are a variety of hydrated aluminosilicates that appear as layers or structures that include polymeric sheets. Clay minerals have received great attention in the past decades due to their properties, such as natural abundance, high reactivity, and low cost [2].

Aluminum is a very important light element that is widely used in many industries, including aviation, automobiles, communications, construction, etc. About 85% of bauxite is used to produce aluminum, 8% of which is used in the production of alumina. Bauxite reserves in the world are concentrated in tropical and subtropical regions, as large deposits in West Africa, Australia, South America, and Southeast Asia [3].

Alumina (Al_2O_3) is considered one of the most supportive materials for chemical catalysts, as it has been used in many fields and for different metals. The porous nature of alumina played an effective role in hindering the sintering of metal (catalyst) particles on its surface through the influence of the various pores in it [4].

Adsorption is a very important industrial process. Alumina has many phases such as gamma (γ), delta (δ), theta (θ), eta (η) and kappa (κ). Alumina can also exist in numerous crystal forms.

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The two alumina, γ and δ, are the main focus. Because of its high surface area and stability across a wide temperature [5].

Nickel catalyst mounted on a support has been widely used in industry, as it has been used to catalyze many beneficial reactions, hydrogenation, and hydrocracking. Studies have shown that the performance and specificity of these catalysts depend on the interaction between the metal and the support, as the difference in support plays a role in the process. Catalysts such as SiO_2, Al_2O_3, MgO, ZrO_2 and TiO_2.Generally, alumina sand is used with these catalysts due to its thermal stability under different reaction conditions. However, the catalyst can malfunction when used in petroleum treatments due to carbon formation reactions, which lead to contamination of the surface of the catalyst, which affects its catalytic behavior. For these reasons, efforts have been devoted to improving the performance of catalysts. Nickel and its support with some noble metals such as Pt, Pd or Rh and other transition metals such as Mo or Co. Nickel molybdate is considered a distinctive catalyst for many reactions, such as hydrotreatment processes, oxidative dehydrogenation (ODH), and selective oxidation of alkanes, and it is considered the most widely used in oil refining [6].

The research aims to produce alumina from natural ore (bauxite), which contains high percentages of aluminum, which is found in large quantities in the Husseiniyat area of Anbar Governorate. Alumina is used as a supporting material for the nickel and molybdenum catalyst in the form ($Ni - Mo/Al_2O_3$) and to study the properties of the catalyst and know its components and identifying its effectiveness using modern technologies.

EXPERIMENTAL

Preparation of the clay ore

The bauxite ore used in the study was selected using the traditional geological method followed by the General Company for Geological Survey in Baghdad, from the upper layer to the lower layer. The ore is found in the form of deposits or irregular blocks in Anbar Governorate, the Husseiniyat area, and this area is considered abundant in bauxite ore.

Preparation of the sample for study

A certain weight of natural ore (bauxite) was taken and ground with a manual mortar (mortar), then sieved using a 200 mesh sieve, then ethanol was added to it while continuing the grinding process to avoid the crystalline structures of the minerals in the model being affected by the heat generated during the grinding process [7].

Steps to prepare the model under study

Removal of carbonates from natural ore

(150 g) of the crude prepared in the previous paragraph was taken and placed in a circular flask with a capacity of 500 mL, and 300 mL of a solution of 10% hydrochloric acid (HCl) was added to it, then refluxing was carried out using a reflector condenser. In a circular flask for 3 hours, then cooled to laboratory temperature, the solution was filtered and the sediment was washed with distilled water several times and dried at 125 ℃ for 5 hours in an electric oven, then placed in a desiccator and after it settled. The purified sample was weighed, and the difference in weight represents the amount of carbonate removed from the natural ore [8, 9].

Iron removal from clay ore

The clay crude treated in the previous paragraph was taken, placed in a 500 mL round-bottom flask and 200 mL of $Na_2S_2O_4$ was added, and the reflux process was conducted with the condenser for a period of two hours and cooled at the laboratory temperature, the solution was filtered, and the precipitate was taken and washed with distilled water and was treated with 200 ml of 10% hydrochloric acid in a 500 mL round-bottom flask, the reflux was made for an hour and the conical flask was cooled to the laboratory temperature, then the sedimentation was filtered, washed with distilled water, then it was dried in an electric oven at a temperature of 120 ℃ for a period of 3 hours, then transferred to a 500 mL beaker, and 100 mL of toluene was added with continuous shaking and heated to a temperature of 70 ℃ for 30 min then filtered and dried at 120 ℃ for a period of two hours, and after the residue was settled, it was weighed, as the difference in the weight represents the amount of iron removed from the mineral crude [10].

Silica removal from clay metal raw

The metal ore sample treated in the previous two paragraphs was taken, placed in a 500 mL round-bottom flask and 250 mL of a solution of 0.5 M sodium hydroxide was added, and it was refluxed under a condenser for 5 hours, then the round-bottom flask left to cool at the laboratory temperature, then filtered and the remaining metal crude was washed with distilled water, then dried at a temperature of 120 ℃ for a period of 3 hours and transported to the dryer (desicator), and after the precipitate stabilizes, the weight was taken, and the decrease in weight represents the amount of noncrystalline silica that turned into sodium silicate [11, 12].

Aluminum oxide preparation from raw (bauxite)

Metal raw sample treated in the previous paragraphs was taken after removing carbonate, iron and non-crystal silica and placed in a 500 mL beaker and 100 mL of distilled water was added with heating and continuous shaking by a mechanical device at a temperature of 70 ℃, then 100 mL of the concentrated sulfuric acid was added drop by drop until the acid was finished and then putted in a 500 mL round-bottom and refluxed under a reflective condenser for one hour and then the solution was left to cool with the laboratory temperature and then filtered with an ashless filter paper number 24 and washed with distilled water several times, then a few drops of pH indicator were added to the filtrate and amended by adding 25% ammonium hydroxide solution drop by drop with constant stirring until the color of the indicator becomes light pink, then the mixture was heated to a boiling point for 10 min, then and left to settle for 15 min and filtered with ashless filter paper number 24 and left to dry at the laboratory temperature for 24 hours and then the precipitate was put in an electric oven at a temperature of 120 ℃ for a period of 5 hours, then transferred with a filtration paper to a crucible and the ignition process was completed with an electric oven 600 ℃ for two hours, after which the weight of the model represented by aluminum oxide (Kama-Alumina) was performed [13-15].

Preparing nickel and molybdenum burden on alumina

Previously prepared (10 g) of Kama-Alumina (alumina) was taken and 1.5 g of ammonium hepta molybdate nickelnitrite was added with 1.34 g of nickel nitrite and 200 mL of distilled water. It was then placed on the mechanical rugged device to stir for one hour, then left for 4 hours and dried up 110 ℃ during a period of 3 hours, and after that, the lunar process was completed at a temperature of 450 ℃ for a period of 4 hours [16].

RESULTS AND DISCUSSION

The bauxite ore and the prepared catalyst were analyzed using X-ray scattering (EDX) technology to determine the elements present in each of them. It was found that the ore consists mainly of the elements aluminum and oxygen, with peaks appearing in low percentages belonging to iron, silicon, calcium, and titanium, as shown in Figure 1. As for the catalyst, we notice a clear decrease in the percentage of silica and carbonates, evidence of actual removal through chemical treatment processes, noting the appearance of clear peaks in small percentages of nickel and molybdenum, indicating that metal loading has occurred on the alumina, as shown in Figure 2.

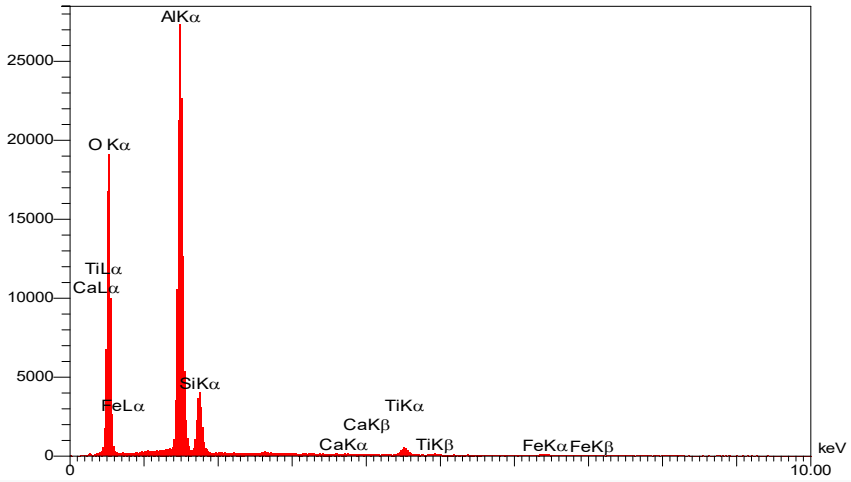

Figure 1. EDX for clay (bauxite).

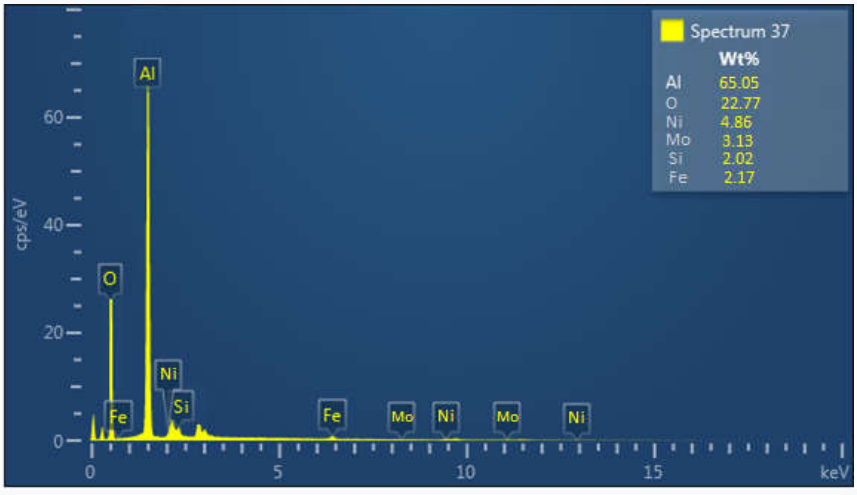

Figure 2. EDX for prepared catalyst (Ni-Mo).

The results of the (FE-SEM) image of the catalyst under study showed that the catalyst grains are more regular and have a crystalline shape with varying sizes. It was also shown that nano-sized catalysts appeared, ranging from (31.97-50.33) nanometers, and this indicates an increase in the selectivity of the nano-sized catalyst, as shown in Figure 3.

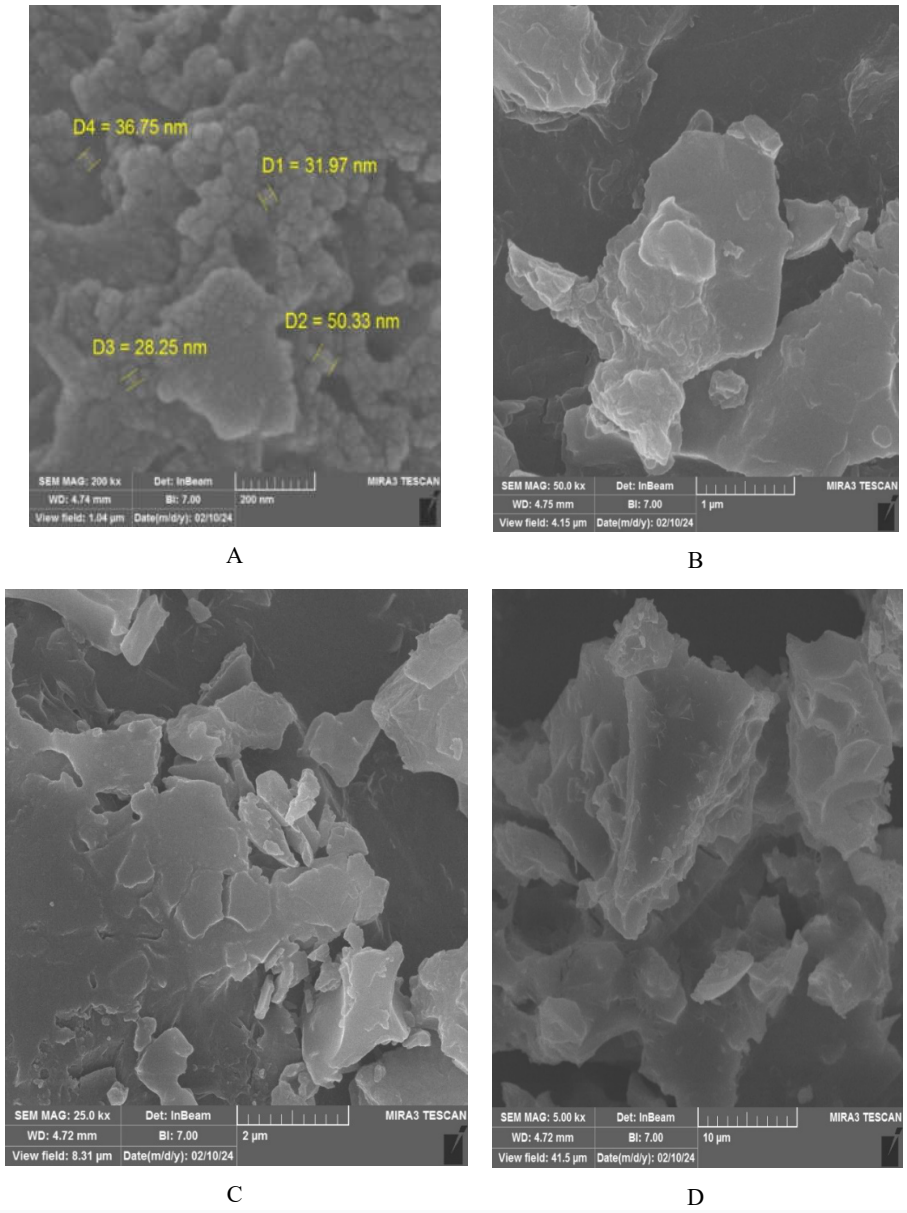

Figure 3. SEM for prepared catalyst (Ni-Mo).

The study of thermogravimetric analysis (TGA) and differential analysis of the prepared catalyst is very important to identify the type of water molecules present in the catalyst (Ni-Mo), as this technique shows the amount of the types of water molecules lost by the catalyst, whether moisture water or water molecules present in the pores. Internal or hydroxyl and carbonate groups. In clayey ore, surface-bound water molecules are lost at a temperature of 110 °C, while water molecules within the porous crystalline structure channels are lost at a higher temperature exceeding 250 °C. Upon raising the temperature to above 350 °C, hydroxyl groups in the internal structure of the ore are lost in the form of water molecules. Each pair of hydroxyl groups is transformed into a water molecule leaving behind a single oxygen atom on the ore's crystalline structure. Furthermore, carbonate decomposition begins by losing CO_2 gas, transforming its elements into an oxidic form after reaching a temperature of approximately 450 °C and continuing up to around 600 °C. Figures 4 and 5 show the measurement of TGA and differential analysis, respectively, for the prepared catalyst.

As for the analysis of the X-ray fluorescence (XRF) technique of the prepared catalyst and bauxite, it turns out that there is a clear change in the proportions of the elements in varying proportions as shown in Table 1, and it turns out that the percentage of silicon and aluminum is the largest percentage in the ore, The reason for the high content of silica (SiO_2) and aluminum (Al_2O_3) in bauxite is that bauxite is primarily composed of aluminum oxide, which is the main component for producing aluminum. Silica is present primarily in bauxite due to natural sediment deposits. Quartz sand (containing silica) may be found in conjunction with bauxite, leading to a high silica content in the ore. Additionally, the content of silica and aluminum in bauxite may vary depending on the quality and source of the ore, influencing the extraction and processing of aluminum from bauxite. Furthermore, Iraqi bauxite ore, currently under study, is characterized by its high content of these elements. But with regard to the catalyst we notice a decrease. It has a large percentage of silica, carbonates, and iron, with percentages of nickel and molybdenum in the oxide form. This confirms the occurrence of a loading process for these catalysts on alumina. This is consistent with the EDX measurement of the prepared catalyst and the raw material used.

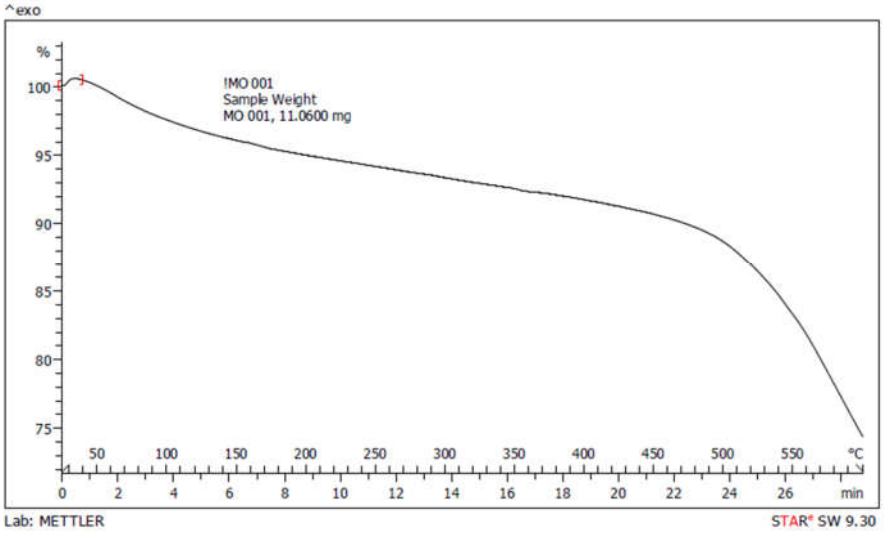

Figure 4. TGA curves for prepared catalyst (Ni-Mo).

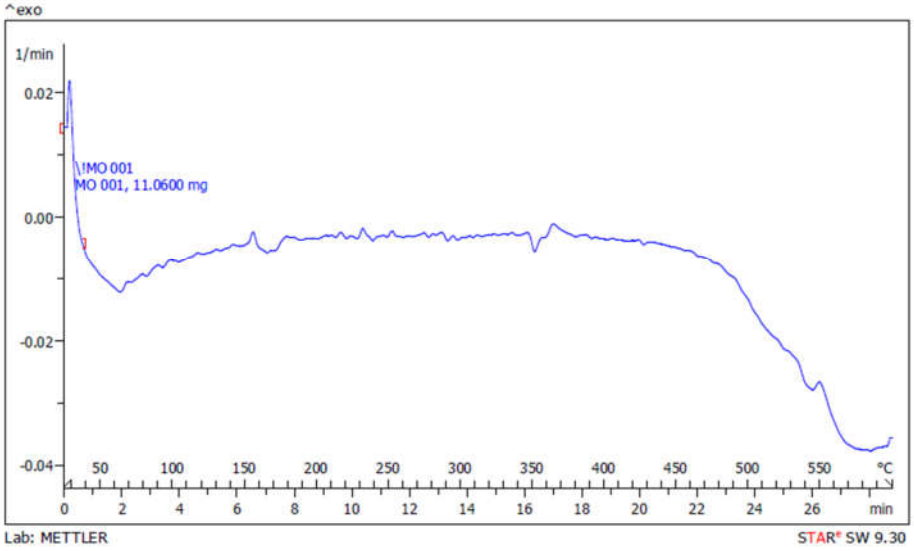

Figure 5. DTA curves for prepared catalyst (Ni-Mo).

Table 1. XRF analysis for bauxite and prepared catalyst (Ni-Mo).

Metal oxides	Percentage ratio (%) of bauxite	Percentage ratio (%) of catalyst
Al_2O_3	52.3	47.67
SiO_2	22.8	10.658
Fe_2O_3	5.973	3.578
CaO	4.336	1.393
V_2O_5	0.289	0.234
TiO_2	5.930	0.058
SO_3	6.91	4.26
NiO	0.0209	7.752
MoO_2	--	3.145
Cr_2O_3	0.0582	0.0255
ZrO_2	0.6473	0.256
CuO	0.0311	0.0147
ZnO	0.0090	0.0039
SrO	0.0215	0.0034
K_2O	0.125	0.1485
MnO	0.0192	--
Y_2O_3	0.0274	--
Ga_2O_3	0.0355	--
Nb_2O_5	0.0857	--
Yb_2O_3	0.017	--
Re_2O_7	0.003	--
IrO_2	0.0052	--
RuO_2	0.356	--

X-ray diffraction (XRD) measurement of the catalyst and ore was carried out in order to determine the content of clay and non-clay minerals, in addition to identifying the specific crystalline patterns of each mineral and comparing them with the standard diffraction patterns (AMCSD, 2023) using the program (X Pert High Score Plus). Figure 6 shows X-ray diffraction of bauxite and shows that bauxite ore contains hydrated aluminum oxides in addition to kaolin, hematite, and calcite. As for the (XRD) measurement of the prepared catalyst, we note that it matches the standard model 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), in addition to the appearance of bands belonging to nickel and molybdenum, as shown in Figure 7 and Table 2.

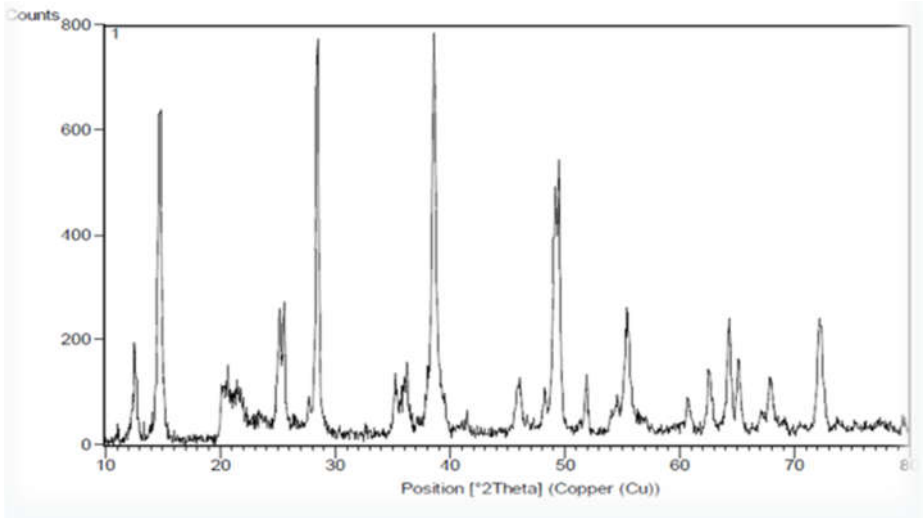

Figure 6. XRD for (bauxite).

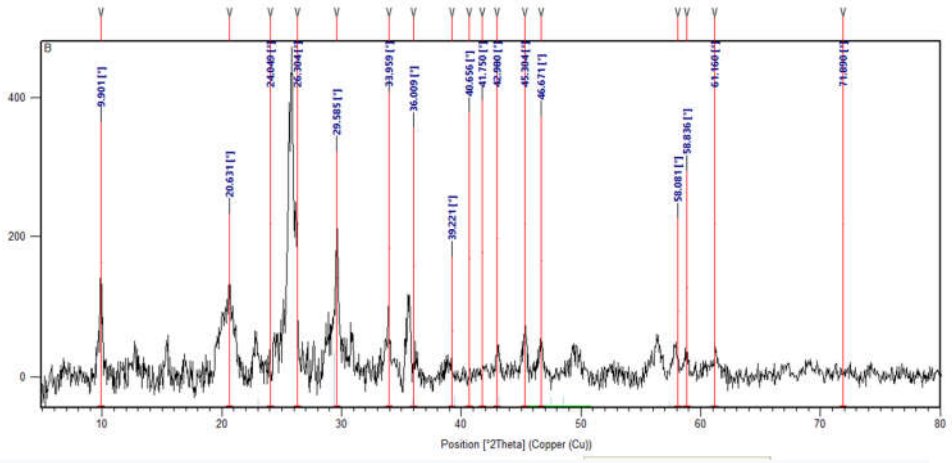

Figure 7. XRD for catalyst (Ni-Mo).

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

Minerals	2θ	d-spacing
Boehmite $AlO(OH)$	9.901 45.39 71.80	0.1355 1.9855 1.3147
Gibbsite $Al(OH)_3$	20.68 46.69	4.3573 1.9336
Nickel	39.26 41.72 58.62	2.2950 2.1650 1.5748
Molybdenum	40.62 58.80	2.2210 1.5705
Quartz SiO_2	26.35 42.47	3.3446 2.1287
Calcite $CaCO_3$	29.52 36.00 61.13	3.0357 2.4950 1.5094
Hematite Fe_2O_3	24.15 33.95	3.6855 2.7028

As for BET analysis, which is a method used in physical chemistry through which the surface area of the prepared catalyst is known, as in Table 3, excellent data were revealed, as the surface area reached (150.568 m^2/g) and was measured by the Langmuir method, Langmuir method is a second method to measure the surface area of the catalyst, which appeared as(645.6078 m^2/g) and relies on the use of the surface equilibrium technique where the surface pressure is measured compared to the flow of gas over the surface under study. Generally, Langmuir method provides accurate results that help in understanding and analyzing surface properties more effectively. The size and diameter of the pores were also measured.

Table 3. BET analysis.

Measurements	Analysis data
BET surface area	150.568 m^2/g
Langmuir surface area	645.6078 m^2/g
Pore volume	0.018567 cm^3/g
Pore size	4.93244 nm

CONCLUSION

It has been shown through measurements and apparent results of the prepared Ni-Mo/Al_2O_3 catalyst that it has a clear crystalline shape, a high surface area, various pore channels, and good thermal stability, in addition to benefiting from the natural mineral ore used as a low-cost, environmentally friendly raw material in preparing the support material (alumina). There is a study that will be published later that shows its catalytic ability in the field of catalytic synthetic reform of the petroleum derivative (naphtha).

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