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RESEARCH PAPER

Preparation and Characterization of Nano Pt-Pd/Al_2O_3 Catalyst from Bauxite Ore

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ABSTRACT

The study includes the selection of one of the natural ores (bauxite clays), which is characterized by its high content of various aluminum minerals such as $Al(OH)_3$ gypsumite, bohemite and AlO(OH) disbor as a source to obtain alumina (Al_2O_3), and using it as a catalyst support material, and then identifying its content of Clay and non-clay minerals, as well as studying its components using various techniques such as X-ray energy dispersion (EDX) technique, X-ray diffraction (XRD) technique, and X-ray fluorescence (XRF) technique. After that, unwanted components that negatively affect the effectiveness of the prepared catalyst, such as carbonates, are estimated and removed. Iron and non-crystalline silica, after which aluminum oxide (alumina) is prepared from the ore through a series of chemical treatments, and then a catalyst consisting of transition elements (platinum and palladium) loaded on alumina is prepared and studied using different techniques, identifying its components, and determining the weight and atomic percentages for each including measuring the energy dispersion of X-rays (EDX) and ensuring its thermal stability by conducting a thermogravimetric analysis (TG) A), differential thermal analysis (DTA), surface area measurement of the prepared catalyst (BET), scanning electron microscopy (SEM), as well as X-ray diffraction (XRD) and X-ray fluorescence (XRF) for the purpose of identifying the percentages of constituent minerals, and then estimating The ratio of these elements in their oxide form.

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INTRODUCTION

Clays are salts in the form of very small granules (particles) with a diameter of (0.002mm), or maybe less than that. They can be produced by fragmentation of rocks or by chemical reactions in the soil after the formation of rocks, where clays are one of the secondary components present in the soil, and its percentage constitutes about (2.02%) of the percentage of the earth's crust, and (12%) of the soil, in addition to the presence of other main components, such as sand, and its percentage is within (0.02-2 mm) i.e. (80%) of the soil mud has chemical and physical properties that differ greatly from sand [1].

Clays contain many clay minerals that have characteristics of many uses and depend greatly on the characteristics and composition of the mineral. In addition, there are several factors that are important for determining the applications and properties of clay, including the presence of

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non-clay minerals and organic materials, and the amount and type of ions that can be exchanged with dissolved salts [2].

The bauxite ore consists mainly of a number of clay and non-clay minerals, and the most important non-clay minerals, which are among the main components, are the minerals boehmite with a chemical composition (AlO(OH)) and disbor (AlO(OH)) and gypsum ($Al(OH)_3$).These minerals are one of the main components of aluminum in bauxite ore, and there are iron element minerals such as hematite (Fe_2O_3) and macnatite (Fe_3O_4), and minerals of both titanium (TiO_2) and quartz (SiO_2). $Al_2O_3.2SiO_2.2H_2O$) and kaolinite ($Al_2Si_2O_5(OH)_4$) [3,4].

Bauxite deposits are located in Iraq in the north of the Husseiniyat region of the Iraqi western desert and are the only known source of bauxite ore in Iraq. They were discovered in 1990 by the Iraqi Geological Survey. Where bauxite is present in the form of lenses whose thickness sometimes reaches about 35 meters in scattered erosion accompanied by kaolinite clays and sandstone. The thickness of the bauxite section may reach 100 meters in most cases [5].

Alumina (aluminum oxide Al_2O_3) can be obtained from bauxite ore, which is one of the most important adsorbents used in the oil industry and in chromatographic separation processes, where the alumina activates at a temperature between (400-600) °C, and the activation of alumina at this temperature is the highest for the surface area, and it is not preferable to heat it more, as the surface area decreases and suffers from the sintering process as the temperature increases .It is possible to lose (15%) of its surface area if the temperature is raised to 734 °C, and it also loses (40%) of that area when heated to 938 °C [6].

Al-Hyali [7] was able to study the catalytic treatment of heavy naphtha (100-200 °C) distilled from Kirkuk crude oil (Jumbour wells) using a palladium catalyst carried on kama alumina obtained from bauxite ore using an autoclave reactor, where the catalytic treatment was carried out. It was prepared by using urea complexes and sulfonation and unsaturation processes to identify the content of straight paraffins and the aromatic and olivine content. The results showed the ability of the catalyst to perform hydrogen removal and reforming operations.

Zaki et al. [8] studied the possibility of conducting the process of synthetic reformation of heavy Iraqi naphtha using a mixed catalyst of bimetallic elements (platinum and titanium) loaded on zeolites, where the process was conducted at a temperature ranging between (490 - 510 °C) and pressure of 10 bar. The study showed that the best result was the octane number (84) using a sample (0.13% for platinum) and (0.75% for titanium) carried on zeolite at a temperature of (510 °C) and a pressure of 10 bar. All catalyst samples also showed stability during the drying process.

Saeed and Salim [9] were able to prepare a palladium catalyst from bauxite ore and use it in the catalytic treatment of kerosene. Synthetic composition of olefin and aromatic compounds. Al-Jawali [10] prepared zeolite catalysts doped with MoO_3 and WO_3 oxides and used them to improve the caustic naphtha. And the formation of aromatic compounds and an increase and decrease in the formation of naphthenic compounds in varying proportions, in addition to an increase in the value of the octane number.

Saxena and De [11] were able to prepare platinum and palladium catalysts loaded on alumina by precipitation and used them to remove hydrogen from butane, as the results showed that bimetallic catalysts have high catalytic capacity and efficiency compared to monometallic ones.

Dong and Yamazaki [12] were able to prepare a platinum-palladium catalyst carried on silica using a colloidal solution of Pt-Pd alloy and used it in diesel oxidation, and it was verified by (EDX) and scanning electron microscopy (SEM), where the catalyst showed catalytic activity higher than the traditional Pt-Pd catalyst prepared from common solutions.

Al-Khafaji [13] used zeolite doped with chromium and cobalt oxides to carry out the synthetic reform process of heavy naphtha for Ajeel crude oil, and after knowing the properties of zeolite prepared from natural clays, it was tested inside an autoclave reactor under different conditions, and the results showed that the best catalyst ratio is 3% and the time the reaction took is three hours at a temperature of 300 °C, and a large increase in the amount of aromatic hydrocarbons was obtained.

MATERIALS AND METHODS

Preparation of the Clay Ore Sample for Study

The study model (bauxite ore) was selected by the traditional geological method used in the

General Company of Geological Survey in Baghdad from the upper layer to the lower layer, where the ore is found in the form of sediments or irregular blocks in the Husseiniyat area in Anbar Governorate, and this area is considered rich in bauxite ore.

Preparing the raw model used in the study

A certain weight was taken from the natural clay ore (bauxite), which was ground with a manual mortar (Mortor) and then sifted using a 200mesh sieve, and ethanol was added to it during the grinding process to avoid the effect of the crystalline structures of the minerals in the model by the heat caused by the grinding process [14].

Steps to prepare and configure the model under study

Removal of carbonates from natural ore

(150) grams of the raw material prepared in paragraph (2.2) were taken and placed in a circular flask with a capacity of (500) ml, and (300) ml of (10%) hydrochloric acid (HCl) solution was added to it Then, the thermal sublimation was carried out under the condenser inverter in a circular flask for (3) hours, .Later, it is cooled to the laboratory temperature, the solution is filtered and the precipitate is washed with distilled water for several times, then it is dried at a temperature of (125 °C) for (5) hours in an electric oven and then placed in the desiccator and when the weight stabilizes, it is taken, where the difference in weight represents the amount of carbonate removed from the mineral ore. [15,16]

Iron removal from clay mineral ores

The treated mineral ore was taken in the previous paragraph, where it was placed in a circular flask with a capacity of (500) ml, and (200) ml of a solution (4%) of sodium dithionite ($Na_2S_2O_4$) was added to it, then the thermal sublimation process was carried out by means of a reflective condenser for a period of (two hours) and then it was cooled to the laboratory temperature, then 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 circular flask with a capacity of (500) ml, and thermal escalation was performed for one 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 coloring was added to it with continuous shaking and heating. This is done to a temperature of (70 °C) for a period of (30) minutes, after that it is filtered and dried at a temperature of (120 °C) for a period of (two hours), and when the weight stabilizes, it is taken. where the difference in weight represents the amount of iron removed from the mineral ore [17].

Removal of silica from clay mineral ores

A sample of the processed mineral ore was taken in the previous two paragraphs, and placed in a circular flask with a capacity of (500) ml, and to it (250 ml) of a solution was added.

(0.5) molar sodium hydroxide, and it was thermally escalated under a reflective condenser for (5) hours, then the flask was left to cool at the laboratory temperature, then the remaining metal 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 settlement of the precipitate, the weight is taken, and the decrease in weight represents the amount of amorphous silica that has been transformed into sodium silicate [18,19].

Preparation of aluminum oxide from mineral ore (bauxite)

The mineral ore sample treated in the previous paragraphs was taken after removing the carbonate, 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 by means of a mechanical device at a temperature of (70 °C), then added (100) ml of concentrated sulfuric acid, drop by drop, until the acid is finished, then placed in a flask with a capacity of (500) ml, and thermal escalation was carried out under a reflective condenser for one hour, then the solution was left to cool to the laboratory temperature, and then filtered using ashless filter paper No. (24). (With distilled water washing several times, then taking the filtrate and adding a few drops of phenolphthalein indicator to it and adjusted by adding ammonium hydroxide solution (25%) drop by drop with continuous stirring until the color of the indicator becomes light pink, then heat the mixture is heated to boiling point for (10) minutes,

then left to settle for (15) minutes, 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 transferred with paper . The filter was transferred to a ceramic lid and the firing process was completed in an oven Electrophoresis at (600 °C) for two hours, after which the model representing aluminum oxide (Kama-alumina) was weighed [20-22].

Preparation of alumina-loaded platinum and palladium catalysts

(25) grams of Kama-alumina powder prepared in paragraph (2.5) were taken in a 500-ml beaker, and (200) ml of hydrazine solution (N_2H_4) was added to it and left for (15) minutes to settle, then the solution was filtered with Ashless filtration paper No. (24), to which (200) ml of (1%) solution of each of palladium chloride solution ($PdCl_2$) and hexa chloroplatinic acid (H_2PtCl_6) was added slowly, and the mixture was mechanically shaken for (5) hours at a temperature (30 °C), then the solution was left to settle for (12) hours, then the filtrate (resulting from the first step of hydrazine filtration with alumina) was added to it with continuous stirring and left to settle for (10) minutes, and the solution was filtered with ashless filter paper No. (24) and washed repeatedly with distilled water until we get rid of the chloride ions, and the detection is done by silver nitrate $AgNO_3$, then the precipitate is dried at (120 °C) and for the purpose of converting the catalyst into the form of granules, it is placed in a beaker with a capacity of (250) ml and an amount of distilled water is added to it, then it is placed in a syringe .It is specially controlled to obtain the granular shape, then it is placed on the watch glass for (24) hours at the laboratory temperature, after which it is dried. The water was heated in an electric furnace at a temperature of (130 °C) for a period of (3) hours to get rid of the water, and then the calcining process was carried out in an electric oven at a temperature of (500 °C) for a period of (4) hours in order to give the catalyst hardness and increase its thermal stability [23-25].

The analyzes carried out on the ore and prepared catalyst

The physical characteristics of the samples of catalyst and ore were studied using the following analytical techniques.

X-ray energy dispersive measurement

An EDX measurement was carried out for each

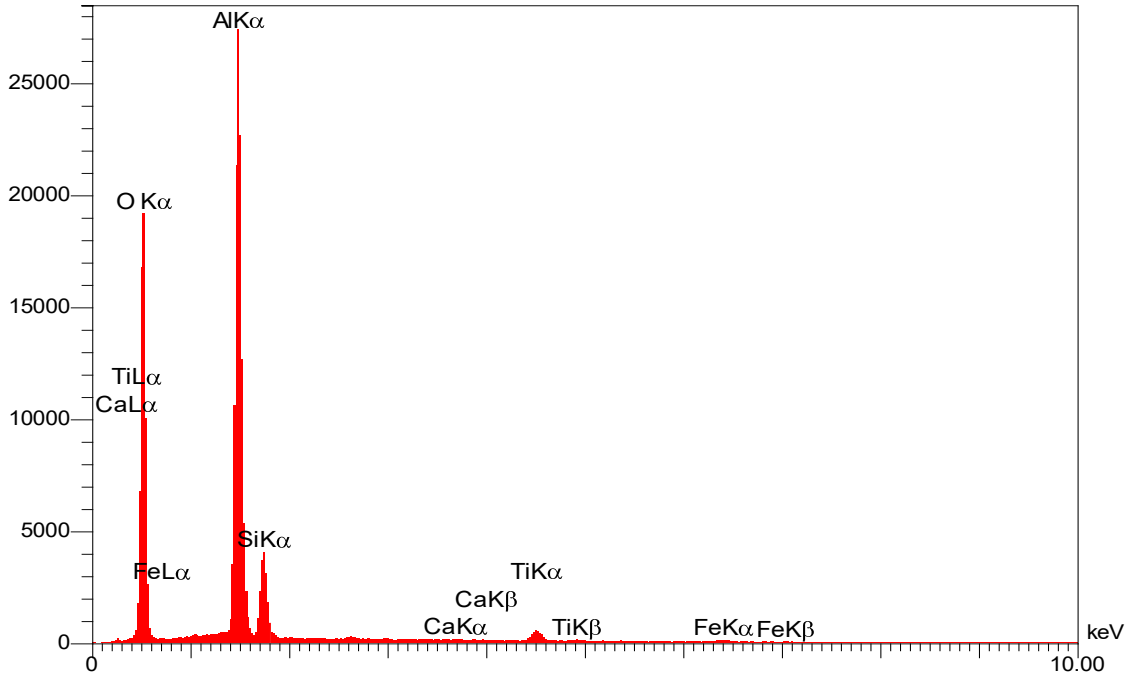

Fig.1. EDX analysis for clay (bauxite)

of the bauxite ore and the catalyst to identify the proportions of their components using an X-ray energy dispersive measurement device, or the so-called analysis for Metals, using a Quanta 200 FEG, FEI Corporata device in Turkey.

Thermo Gravimetric Analysis (TGA (

The thermogravimetric analysis of the prepared catalyst was performed using an apparatus TOLEDO TGA/DSC (METTLER) at the University of Mosul - College of Basic Education - Department of Science.

Differential Thermal Analysis (DTA (

Differential thermal analysis of the prepared catalyst was carried out using METTLERTOLEDO apparatus and software.University of Mosul - College of Basic Education - Department of Science.

X-ray diffraction measurement

X-ray diffraction of the prepared bauxite ore and catalyst was measured using an XPERT PHILLIPS HOLLAND device at Kashan University - Islamic Republic of Iran.

X-ray fluorescence measurement

X-ray fluorescence measurement was performed for each of the prepared ore and catalyst using a (minimal 4) device manufactured by (Panalytical) in the Northern Cement Moawania / Nineveh Governorate.

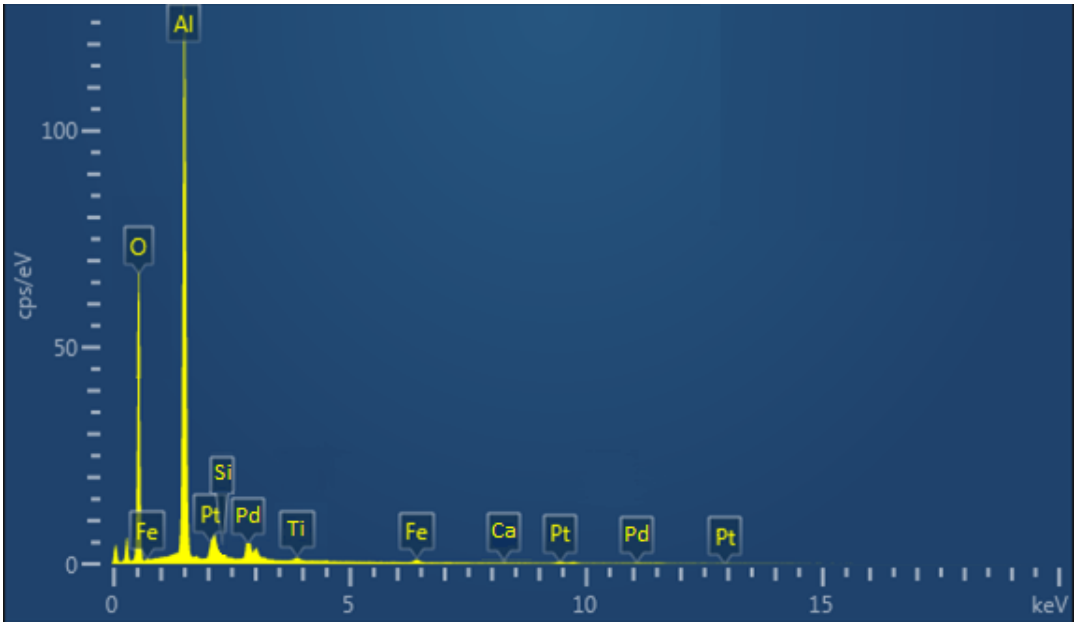

Fig. 2. EDX for prepared catalyst (Pt-Pd)

Table 1. Weight percentages of the different elements present in the catalyst from (EDX)

Element	W%
Al	61.52
O	28.92
Si	0.81
Ti	0.39
Fe	0.56
Ca	0.44
Pd	4.21
Pt	3.15
Total	100

Surface area measurement

A BET measurement was performed to determine the surface area, diameter and pore size of the prepared catalyst using a Nano SORD device at Tehran University - Islamic Republic of Iran.

Scanning electron microscope measurement (SEM)

Scanning electron microscopy (SEM) of France FeSEM Tescan Mira3 of the prepared catalyst was carried out in order to describe an accurate image of the catalyst surface.

RESULTS AND DISCUSSION

Both the bauxite ore and the catalyst prepared by X-ray scattering technique (EDX) were studied for the purpose of identifying the elements present for each of them. It is noted that the ore consists mainly of aluminum and oxygen, as shown in Fig. 1. As for the catalyst, we notice

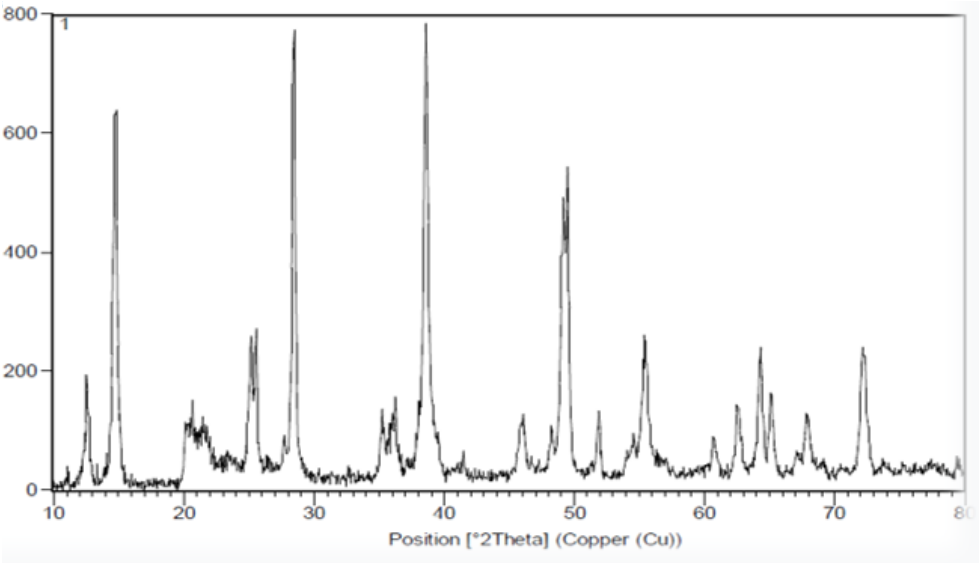

Fig. 3. XRD for for clay (bauxite)

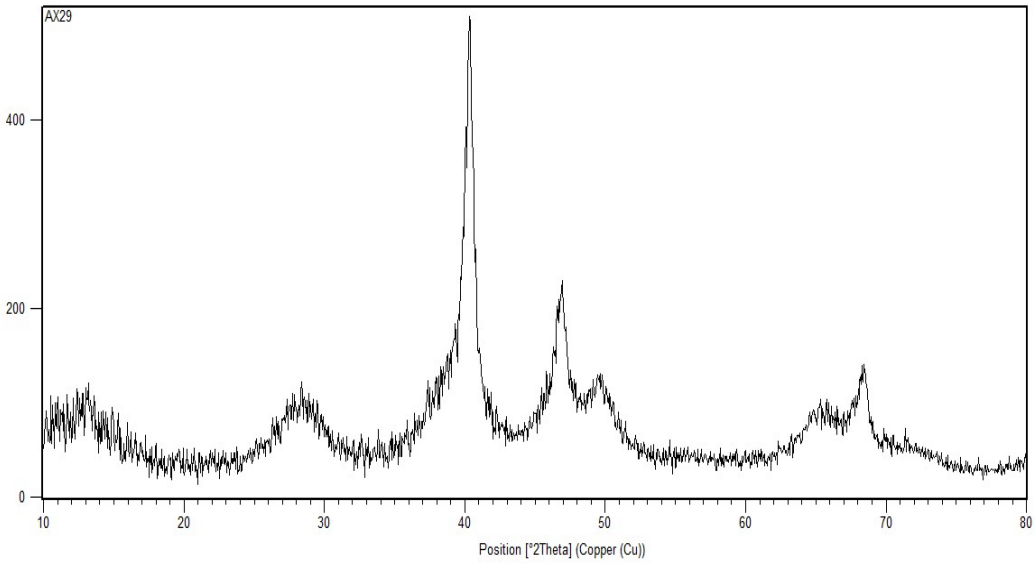

Fig. 4. XRD for prepared catalyst (Pt-Pd)

a clear decrease in the percentage of Silica and carbonates are an indication of actual removal, with the appearance of clear bands of platinum and palladium, indicating that each of them has been loaded on alumina, as shown in Fig. 2 and Table 1. As for measuring the X-ray diffraction (XRD) technique, the purpose is to know the content of clay and non-clay minerals, as well as to identify the crystal patterns of each mineral and match them with the standard diffraction patterns

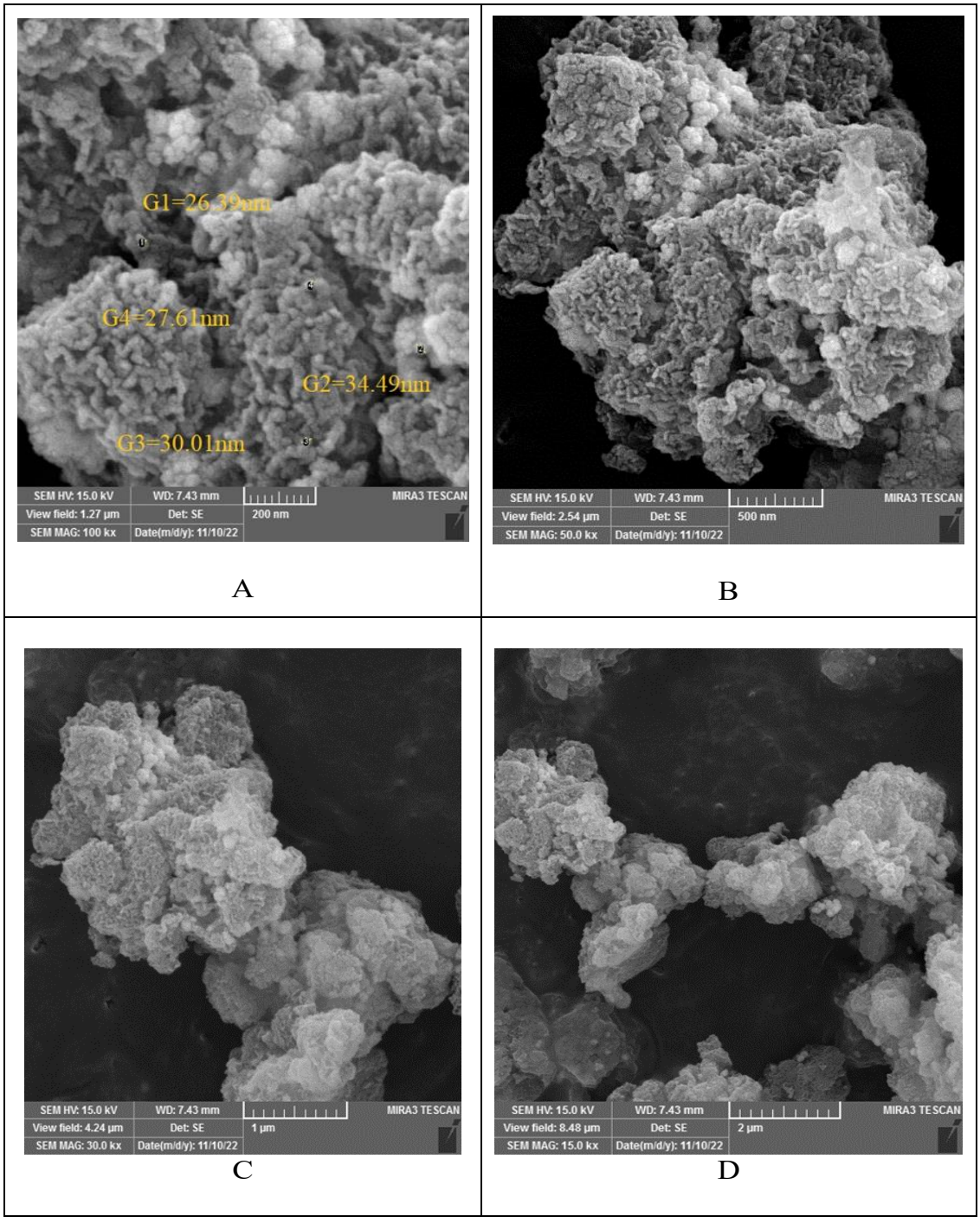

Fig. 5. SEM pictures for prepared catalyst (Pt-Pd) (A = 200nm, B = 500nm, C = 1 µm, D = 2 µm)

(database), as shown in Fig. 3, where we note that the bauxite ore under study contains aqueous aluminum oxides in addition to kaolin, hemite and calcite. While the results of X-ray diffraction measurement of the prepared catalyst consisting of alumina loaded with platinum and palladium showed a perfect match with the standard model of alumina by comparing the diffraction patterns and values of atomic distances (d-spacing) and angles (2θ) that belong to aluminum oxides (bohmite and gypsum), as well the emergence of bundles belonging to platinum and palladium, as shown in Fig. 4.

As for the results of the (SEM) image of the

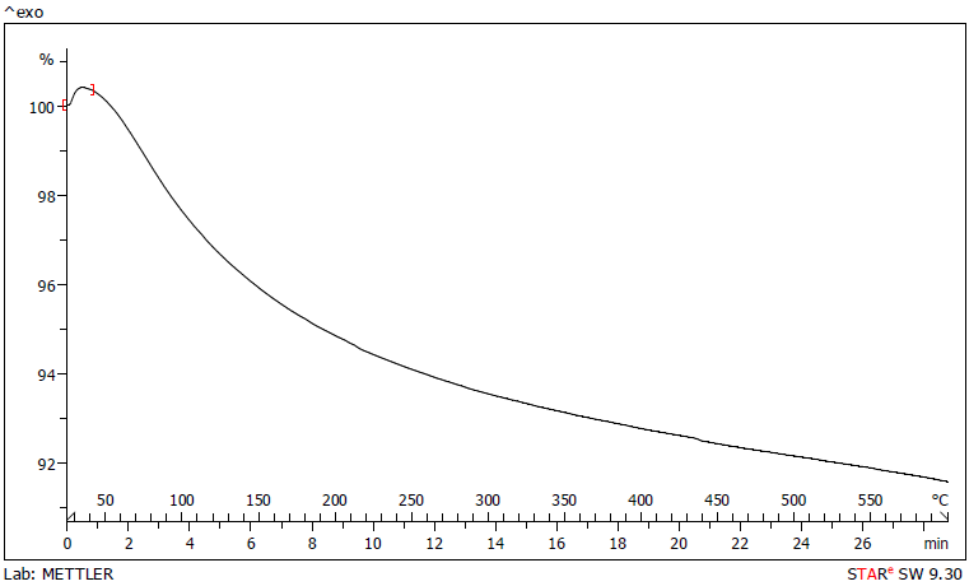

Fig. 6. TGA curves for prepared catalyst (Pt-Pd)

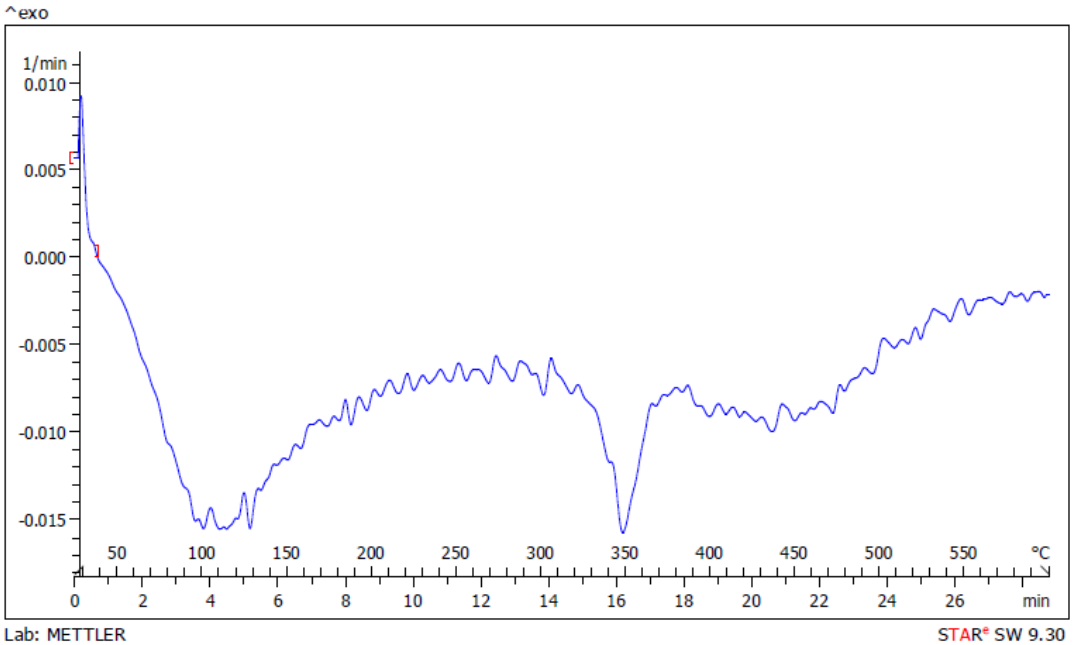

Fig. 7. DTA curves for prepared catalyst (Pt-Pd)

prepared catalyst, the results show that the catalyst granules are more regular, crystalline, and of varying sizes. and by analyzing the (imagej) program, it was observed that the nano-sizes of the prepared catalyst ranged between (26.39-34.49nm). this indicates an increase in the selectivity of the nano-sized catalyst. As in Fig. 5. Moisture water or water molecules present in the internal pores or hydroxyl groups and carbonates at different thermal ranges as shown in Figs. 6 and 7. In the analysis of the X-ray fluorescence (XRF) technique for the catalyst and ore, a change in the

Table 2. XRF analysis for clay, bauxite and prepared catalyst (Pt-Pd)

Metal Oxides	Percentage Ratio (%) of bauxite	Percentage Ratio (%) of Catalyst
SiO_2	25.6	9.389
Al_2O_3	53.3	60.4
CaO	4.336	1.89
V_2O_5	0.289	0.1016
Fe_2O_3	3.973	2.364
K_2O	0.125	--------
SO_3	5.11	1.24
TiO_2	5.930	0.276
Cr_2O_3	0.0582	0.0784
MnO	0.0192	-------
NiO	0.0209	0.0122
CuO	0.0311	0.0458
ZnO	0.0090	------
Ga_2O_3	0.0355	------
SrO	0.0215	------
Y_2O_3	0.0274	------
ZrO_2	0.6473	------
Nb_2O_5	0.0857	------
Yb_2O_3	0.017	------
Re_2O_7	0.003	------
IrO_2	0.0052	------
RuO_2	0.356	0.333
PtO_2	------	10.62
Pd0	------	13.25
Total	100	100

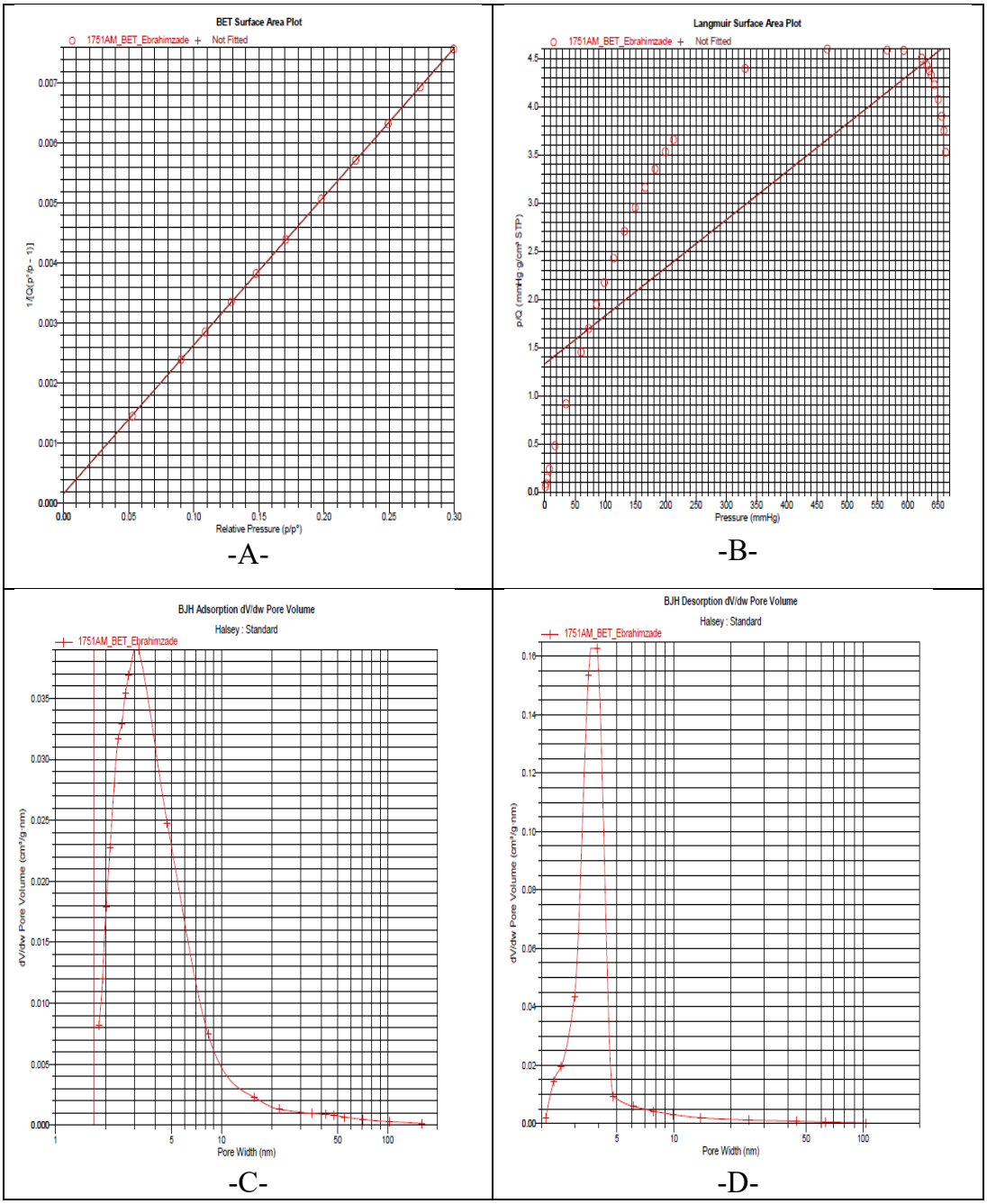

Fig. 8. A) Surface area by BET method B) Surface area by Langmuir method

Table 3. BET analysis

Measurements	Analysis Data
BET Surface Area	174.6326 m^2/g
Langmuir Surface Area	873.5304m^2/g
Pore Volume	0.221597 cm^3/g
Pore Size	5.07574 nm

ratios of the elements is noted as shown in Table 2, and it also shows that the ratio of silica and alumina is higher, and a significant decrease is noticed in the proportion of silica and carbonates with the appearance of values belonging to platinum and palladium, which confirms the process of loading these minerals on the alumina sand, and the BET analysis of the prepared catalyst as shown in Table 3 and Fig. 8 determines the surface area and the size of the pores in the sample, where the surface area was (174.6326 m²/g).

CONCLUSION

1- The results showed that the catalyst has a high surface area (174.6326 m²/g) by Langmuir method (873.5304 m²/g), due to the use of alumina as a support material for the catalyst.

2- The catalyst consists mainly of aluminum and oxygen (aluminium oxide) with the presence of low bands belonging to platinum and palladium loaded on alumina.

3- By studying the electron microscope, it was found that the catalyst consists of granules of varying sizes and good porosity as a result of the presence of voids between the granules and layers.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Appendix A Major legislative changes in unemployment support policy, 1980–2004 (Germany). Reforming European Welfare States: Oxford University PressOxford; 2005. p. 196-197.
2. Wilson I. Applied Clay Mineralogy. Occurrences, processing and application of kaolins, bentonite, palygorskitesepiolite, and common clays. Haydn H. Murray. Developments in Clay Science, volume 2, Elsevier Science, Amsterdam, (2007), 180 + viii pp. ISBN-13: 978-0-444-51701-2, ISBN-10: 0-444-51701-4. Price: USD $145, EUR £120, GBP £83. Clays Clay Miner. 2007;55(6):644-645.
3. Our mineral supplies--Bauxite and aluminum. US Geological Survey; 1919.
4. Meyer FM. Availability of Bauxite Reserves. Natural Resources Research. 2004;13(3):161-172.
5. Al-Bassam KS, Tamar-Agha MY. Genesis of the Hussainiyat ironstone deposit, Western Desert, Iraq. Mineralium Deposita. 1998;33(3):266-282.
6. Holt W. High-temperature combustion of pulverized coal. [Ph. D. Thesis]. Office of Scientific and Technical Information (OSTI); 1982 1982/02/01.
7. Abdullah MA. Study the Mechanical Properties of (Al-Cu-Mg) Matrix Composites Reinforced by Alumina Particles. Tikrit Journal of Pure Science. 2023;20(3):156-161.
8. Ahmedzeki NS, Al-Tabbakh BA, Antwan MB, Yilmaz S. Heavy naphtha upgrading by catalytic reforming over novel bi-functional zeolite catalyst. Reaction Kinetics, Mechanisms and Catalysis. 2018;125(2):1127-1138.
9. Saeed W, Salim Q. preparation of palladium Catalyst from bauxite ore and using for kerosene treatment. JOURNAL OF EDUCATION AND SCIENCE. 2021;30(1):126-140.
10. Use of zeolite NU-86 for naphtha catalytic cracking. Focus on Catalysts. 2020;2020(6):7.
11. Saxena R, De M. Enhanced performance of supported Pd-Pt bimetallic catalysts prepared by modified electroless deposition for butane dehydrogenation. Applied Catalysis A: General. 2021;610:117933.
12. Dong F, Yamazaki K. The Pt-Pd alloy catalyst and enhanced catalytic activity for diesel oxidation. Catal Today. 2021;376:47-54.
13. Meza L, Alvarado JG, Márquez R, Forgiarini A. Performance Evaluation of Demulsifier Using the Optimum Formulation HLD Concept: A Practical Case Using Heavy Crude Oil Diluted in Naphtha or in Synthetic Aromatic Oil. SPE Journal. 2022;27(04):1856-1868.
14. Pansu M, Gautheyrou J. Handbook of Soil Analysis. Springer Berlin Heidelberg; 2006.
15. Loeppert RH, Suarez DL. Carbonate and Gypsum. SSSA Book Series: Soil Science Society of America, American Society of Agronomy; 2018. p. 437-474.
16. Baba AA, Adekola FA. A study of dissolution kinetics of a Nigerian galena ore in hydrochloric acid. Journal of Saudi Chemical Society. 2012;16(4):377-386.
17. Gougazeh M. Removal of iron and titanium contaminants from Jordanian Kaolins by using chemical leaching. Journal of Taibah University for Science. 2018;12(3):247-254.
18. Niibori Y, Kunita M, Tochiyama O, Chida T. Dissolution Rates of Amorphous Silica in Highly Alkaline Solution. J Nucl Sci Technol. 2000;37(4):349-357.
19. Highly Selective Adsorption and Recovery of Palladium from Spent Catalyst Wastewater by 1,4,7,10-Tetraazacyclododecane-Modified Mesoporous Silica. American Chemical Society (ACS).
20. Gougazeh M, Kooli F, Buhl JC. Removal Efficiency of Basic Blue 41 by Three Zeolites Prepared from Natural Jordanian Kaolin. Clays Clay Miner. 2019;67(2):143-153.
21. Stevenson, Timothy Edwin Paul, (born 14 May 1948), Lord-Lieutenant of Oxfordshire, since 2008; Chairman, Johnson Matthey plc, since 2011. Who's Who: Oxford University Press; 2007.
22. M. Al-Mukhtar A-S, Y. Al-Dabbagh N, S. Al-Sherrefat N. MICROSPORIDIOSIS IN MALIGNANCY AFFECTED PATIENTS IN MOSUL, IRAQ. The Medical Journal of Basrah University. 2008;26(1):28-31.
23. Kim HS, Kim TW, Koh HL, Lee SH, Min BR. Complete benzene oxidation over Pt-Pd bimetal catalyst supported on γ-alumina: influence of Pt-Pd ratio on the catalytic activity. Applied Catalysis A: General. 2005;280(2):125-131.
24. Rodriguez AA, Williams CT, Monnier JR. Selective liquid-phase oxidation of glycerol over Au–Pd/C bimetallic catalysts prepared by electroless deposition. Applied Catalysis A: General. 2014;475:161-168.
25. Babu NS, Lingaiah N, Gopinath R, Sankar Reddy PS, Sai Prasad PS. Characterization and Reactivity of Alumina-Supported Pd Catalysts for the Room-Temperature Hydrodechlorination of Chlorobenzene. The Journal of Physical Chemistry C. 2007;111(17):6447-6453.