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Preparation and Characterization of Metal Carbide Zeolite Composite Catalysts

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Abstract

The object of present work is to synthesize metal carbide zeolite composite catalysts and discusses their characteristics. Metal carbide with zeolite composite was prepared in the present research. Molybdenum carbide was used as a metal carbide which was prepared by solid-state method with Ammonium molybdate tetrahydrate and commercial activated carbon as raw materials. Ion exchanged method was used to add platinum to the HY zeolite. Modified Y zeolite was prepared by using ion exchanged method by mixing the HY zeolite with Cerium nitrate. After prepared Mo₂C, PtHY zeolite, and CeY a formation process take place in order to form two catalysts the first one is Mo₂C/PtHY-Zeolite, while the second one is Mo₂C/CePtY zeolite. Tests such as X-Ray Diffraction, Brunauer-Emmett-Teller (BET) surface area analysis, Fourier transform infrared spectroscopy (FTIR), and Thermal Gravimetric Analysis (TGA) were performed on both catalysts and the results were as follows for the molybdenum carbide the surface area was 1072 m²/g, with a pore volume of 0.541 m³, the TGA indicated that 19.58 wt% of the substance was lost, finally, the average particle size is 18.65 nm.

For the Mo₂C/PtHY-Zeolite catalyst, the BET surface area was 724.55 m²/g, then the Thermal Gravimetric Analysis resulted in 10% of the catalyst being lost, and lastly, the average crystal size was 33.45nm.

Moreover, for Mo₂C/CePtY catalyst, the BET surface area was 734.55 m²/g, then the Thermal Gravimetric Analysis resulted in 19% of the catalyst being lost, and the average crystal size was 40.43nm.

1. Introduction:

Platinum (Pt), while being costly, is a necessary catalyst material for many reactions with industrial uses because of its activity and stability [1]. One such method is continuous catalytic reforming, which has been used in the petroleum industry for over seven decades and uses platinum as an active metal component. In fact, this expensive metal accounts for more than 90% of the total cost of the catalyst. So, examining other metals and materials have activity and stability that can be compared with this noble metal, became an urgent need. Carbon is incorporated into the interstitial sites of transition metals to generate transition metal carbides (TMC) (add reference). These carbide samples show unusually blended ionic crystals, covalent solids, and transition metal characteristics. These substances have high melting points and electrical characteristics comparable to ionic solids, are tougher than covalent solids, and are thermally stable same as transition metals [2]. The transition metals' lattice is enlarged and their metal-metal bond distance is increased by the addition of carbon. Theoretical estimates indicating, in TMCs, charge transfer from metal to carbon cause constriction of the d-band and movement of the density of states for the Fermi level related to its parent metal are supported by experimental findings [3]. These TMC materials have characteristics like to those of the Pt group metals because their electronic states are close to the Fermi level [4]. Due to these special qualities, experts from all over the world are very interested in carbide materials. Under the tested experimental settings, these non-noble materials are used as replacements for expensive metals like Platinum, on a personal level with the Platinum-based catalyst, in the reactions of the oxygen reduction process, isomerization, hydro-deoxygenation, and hydrogenation [5-7]. As was already mentioned, TMC materials like tungsten and molybdenum carbides have been effectively used as catalysts for the important metal-based isomerization and dehydrogenation processes in naphtha reforming. Yet, unlike the noble metal Pt which did not work unsupported, transition metal carbide can be employed unsupported, which may explain why the catalyst behavior is not similar to that of Pt. Even though, (TMC) are sharing the same electrical structure as platinum, to be active for the reactions [8]. The majority of research on carbide catalysts is motivated by Levy and Boudart's significant work [9]. Who hypothesized that out of the eight group metals, except for Cu and Au, Pt, Ir, and Au can catalyze the isomerization of 2,2-dimethylpropane to 2-methylbutane. In order to serve as the counter electrode in dye-sensitized solar cells, Wu et al. [10] produced composites of MoC embedded in order nano mesoporous carbon materials. The characterization revealed that MoC electrodes had a larger positive potential than Pt electrodes. The MoC-based electrode, in contrast side, produced an 8.34% energy conversion

efficiency, which is greater than Platinum (7.98%), according to the photocurrent-voltage experiment. Their findings suggested that molybdenum carbide may be used in place of the precious Platinum counter electrode. According to Chen et al. [11], MoC supported by Al₂O₃ was used in the hydrazine decomposition reaction. The findings of the experiment demonstrated that Mo₂C/-Al₂O₃ catalysts had an outstanding catalytic performance for the decomposition of hydrazine. Additionally, the catalytic activity was equivalent to that of noble metal. Ir. Ji et al. [12] researched supported molybdenum carbide catalysts for catalyzing the conversion of cellulose to polyols, particularly EG (ethylene glycol). According to their findings, the conversion of cellulose by Pt/AC (active carbon) was modest, at 66%, while the AC-supported MoC catalyst resulted in better conversion of the cellulose (85%). Those findings are also suggested that Molybdenum Carbide might serve as an affordable replacement catalyst for Pt noble metal catalysts [13].

High selectivity is another benefit of using molybdenum carbide as a catalyst. Molybdenum carbide frequently exhibits distinctive catalytic pathways, resulting in desired product selectivity, as a result of the electron redistribution once carbon is introduced into the molybdenum bulk. For instance, Han et al. [14] revealed that the molybdenum carbide (Mo₂C/AC) supported nano-sized active carbon may effectively catalyze the conversion of renewable oils in the hydrocarbon mixtures that resemble diesel. The selectivity of olefins on Mo₂C/AC catalyst when the stearic acid was the substrate was significantly greater (85.8%) than that of the Pd nanoparticle catalyst (77.4%). Molybdenum carbide was also explored by Qin et al. [15] as a catalyst for the hydrodeoxygenation of vegetable oils. and discovered that the Mo₂C/CNF (carbon nanofiber) catalyst resulted in good selectivity and activity, and the catalytic performance exhibited no discernible decrease after being recycled five times table (1) will show the basic advantage and disadvantages of molybdenum carbide.

The object of present work is to synthesize metal carbide zeolite composite catalysts and discusses their characteristics.

2. Experimental work

2.1 Materials

Table (1) shows all the chemicals was used in this study, and Table (2) illustrate the advantages and disadvantages of the molybdenum carbide.

Table (1) The chemical compounds used in this study

Chemicals	Formula %	Molecular weight Gm/gmol	Purity	Supplier
Activated carbon	C	12.011	100	SIGMA - ALDRICH
HY-zeolite	SiO ₂ /Al ₂ O ₃	162.05	99	KOMPASS
Ammonium Molybdate tetrahydrate	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O	115.03	99	ROMIL
Hexachloroplatinic acid	H ₂ PtCl ₆ .6H ₂ O	517.92	40	REIDL
Cerium nitrate	CeN ₃ O ₉ .6H ₂ O	434.22	99	SIGMA - ALDRICH

Table (2) Molybdenum carbide Advantages and disadvantages

Advantage	Disadvantage
Unique surface characteristics	Low surface area
High catalytic activity	Formation of the coke on the surface
the selectivity is high	Oxides easily, even at room temperature
Cheaper than Pt-group noble	
High sulfur and nitrogen tolerance metal catalyst	

2.1.1 Preparation process of Molybdenum carbide

Solid-state synthesis was used to create molybdenum carbide supported on activated carbon. In a standard procedure, activated carbon was added to the metal salt solution and agitated by a heating and magnetic stirrer (the stirrer has a thermometer that can adjust the temperature and keep it constant at a certain degree) for two hours at 130 degrees Celsius, followed by solvent evaporation and drying in a 150 C oven for 4 hours Prepared Solid-state reaction carbide materials uniformly combined the carbon and metal precursor were heated at three different temperatures of 800 ,900 & 1000 degrees Celsius at a ramp rate of 4.5 C/h under nitrogen flow and stay at those temperatures

for two hours. The catalyst was cooled to room temperature after the reaction. Figure (1) shows the steps and tubular furnace that used to calcinate the substance.

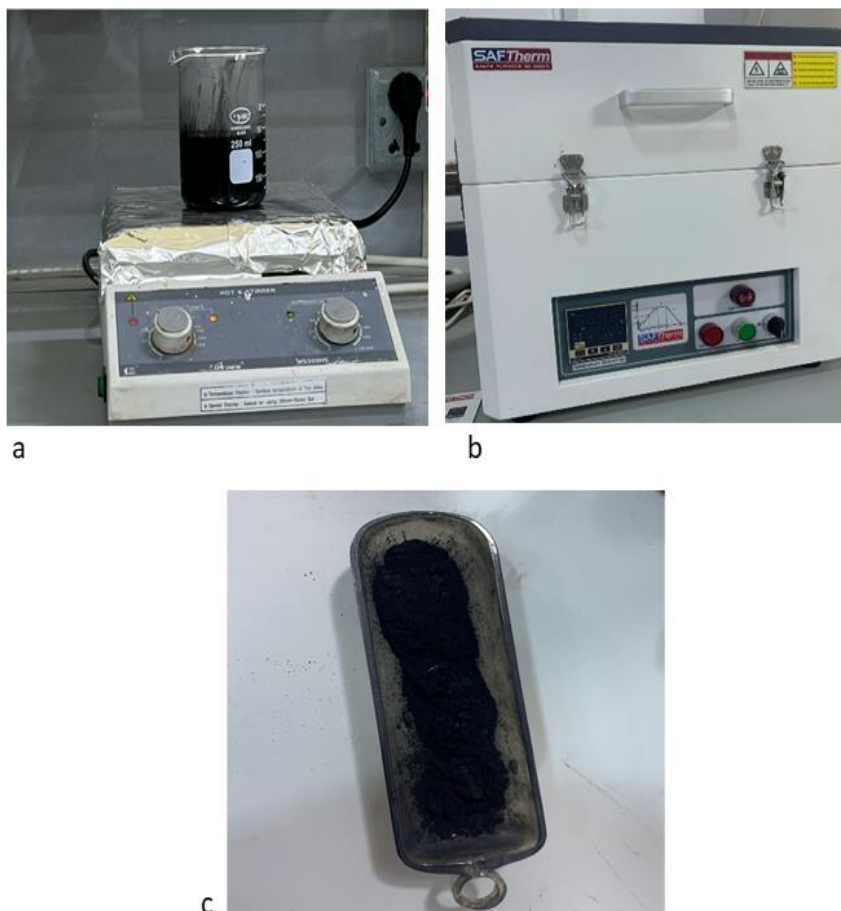
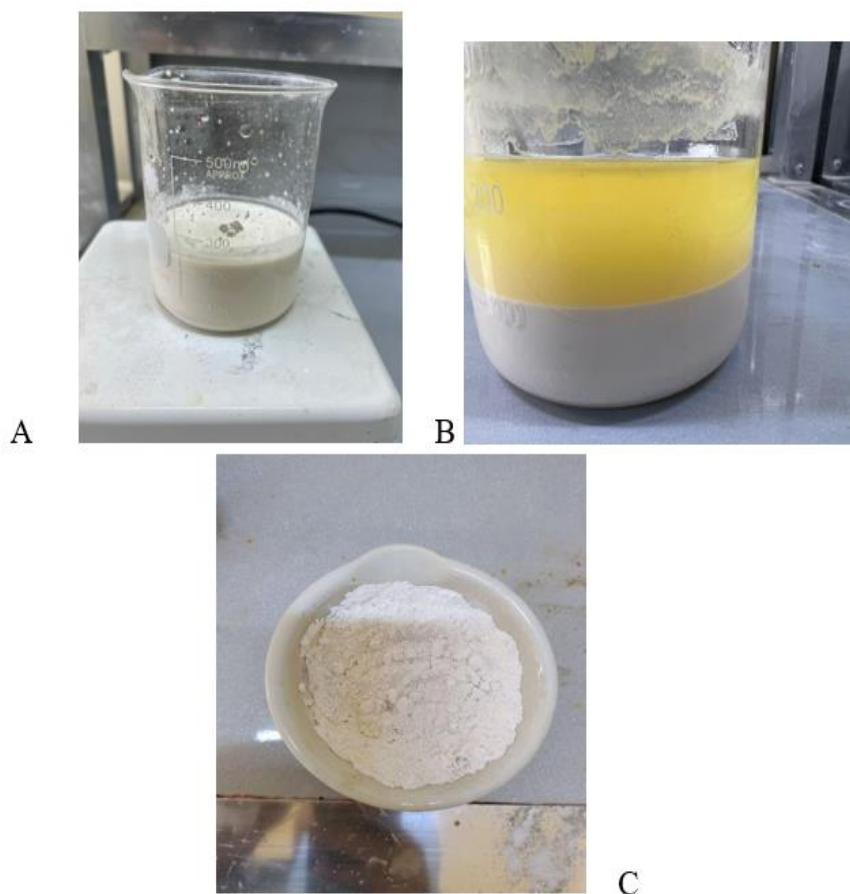


Fig. (1): a- Heating and stirring of the solution, b- Calcination in the tube furnace, c- final Product

2.1.2 Preparation of Platinum supported on HY-Zeolite:

0.43gm of hexachloro platinum acid was added to 175ml of distilled water at room temperature, then 70 g of HY-Zeolite was added to the solution and stirred for 30min without exposing it to heat and leaving the solution to sedimentation until the next day. After one day the solution was filtered, washed, and then entered into a drier to evaporate all water from it. The white powder reduced from this procedure was calcinated at 260°C for 3hr. The percentage of Platinum is 0.25% to HY-Zeolite. Figure (2) shows the steps of the procedure.



**Fig. (2): Preparation of Pt/HY-Zeolite: A. stirring of the solution, B. After 1day
C. After calcination**

2.1.3 Preparation of CePtY

- **Modification of HY zeolite**

The powder of zeolite HY was modified by ion exchange via nitrate solutions of cerium cation $\text{Ce}(\text{NO}_3)_3$ with a certain concentration. The sample is exchanged at 80 °C for 8 hours in accordance with the previously mentioned ratio of 50 g Zeolite HY to 600 mL nitrate solution, after which they were all filtered, washed, dried at 120 °C for 8 hours, and then calcined at 600 °C for 5 hours to produce a Ce modified Zeolite Y.

- **Loaded Pt on the prepared CeY modified zeolite**

0.25% is the percentage of the platinum in this catalyst. 0.14 g of hexachloroplatinic acid dissolved in distilled water inside the separated funnel then Add the powder after calcination to a flask and vacuum the air out of it and then start adding the solution slowly as in Figure (3) then mix it well

and leave it to the next day. After that the substance was washed, filtered, and dried then it entered the furnace at 600°C for 6hr [16]. Figure (3) shows the steps of the procedure.

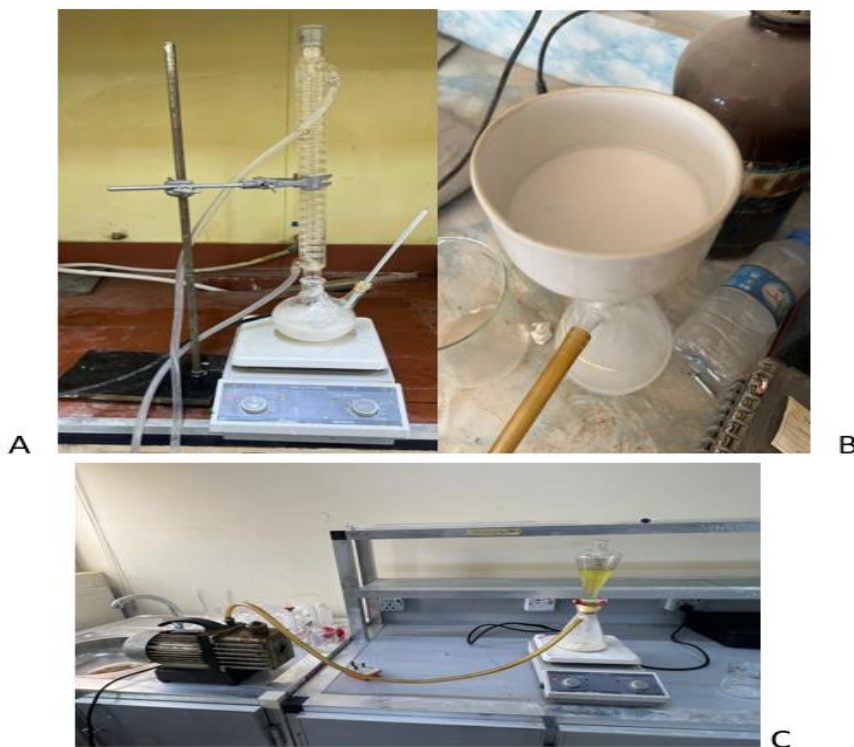


Fig. (3): Preparation of Pt/Ce/HY-Zeolite: A. ion exchange, B. Washing and filtering C. Add the Pt to the powder

2.1.4 Composite catalyst

The final catalyst preparations are shown as "carbide/support.". For optimizing Mo₂C/metal loaded zeolite, it is represented as below:

- Catalyst 1 Mo₂C / PtHY zeolite catalyst.
- Catalyst 2 Mo₂C / CePtY zeolite Catalyst.

3. Results and Discussion

3.1 Molybdenum carbide Mo₂C

1. X-Ray Diffraction

Figure (4) shows the XRD data of the prepared molybdenum carbide. There are molybdenum-indexed peaks in $2\theta = 20.549, 27.734, 31.836, 39.229, 42.827, 56.967, 61.665, 71.676, 73.939$. showing a high level of crystallization for the band of 2θ from 20° to 75° for the produced substance on the XRD analysis. By comparing the sharp peak at 2θ equal to 42 with Hodala et. all. [1] which

has the same peak at 2θ equal to 40. Using Scherrer's equation, the crystal size L was determined as follows.

$$B(2\theta) = \frac{K \gamma}{L \cos\theta}$$

Where:

B : is the FWHM of the peak at 2θ .

K : is the Scherrer's constant, which can range from 0.6 to 2.08 depending on the crystal form; here we consider it [1].

Scherrer's equation applied to X-ray diffraction data yields an average crystal size for Mo_2C of 18.65 nm.

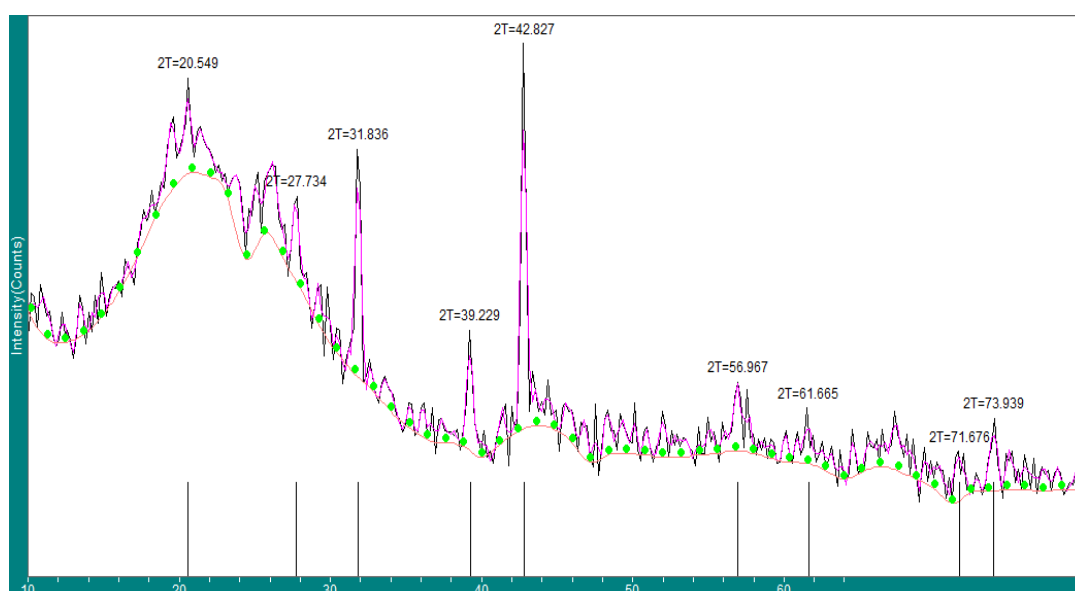


Fig. (4): XRD of the molybdenum carbide

2. BET surface area and Bore volume analysis

The prepared molybdenum carbide had a surface area of $1029.787 \text{ m}^2/\text{g}$ and which is better than Hodala et al. [1] who synthesized molybdenum carbide at 800°C and got a surface area of $835 \text{ m}^2/\text{g}$ [1]. The pore volume of the prepared molybdenum carbide was $0.514 \text{ cm}^3/\text{g}$. A large surface area is due to the raw materials that used to prepare molybdenum carbide. This means it has huge macroporous particles and little mesoporous particles, which means more spaces among particles.

3. Fourier transform infrared spectroscopy FTIR

The chemistry of the surface of the catalyst was considered by the infrared method as shown in Figure (5). The region between $3465\text{--}3889\text{ cm}^{-1}$ reveals the OH stretching on the catalyst, the bands in the range of $2373.22\text{--}2344.89\text{ cm}^{-1}$ indicate the presence of H_2O , so long as the band at about 1558 cm^{-1} assigned to $(\text{COOH}, \text{CH}_2, \text{COO})$ at the surface of the catalyst. The bands in 1077 cm^{-1} reveal to C-O bond. This is the same result was obtained by Yu J. et al. [17]

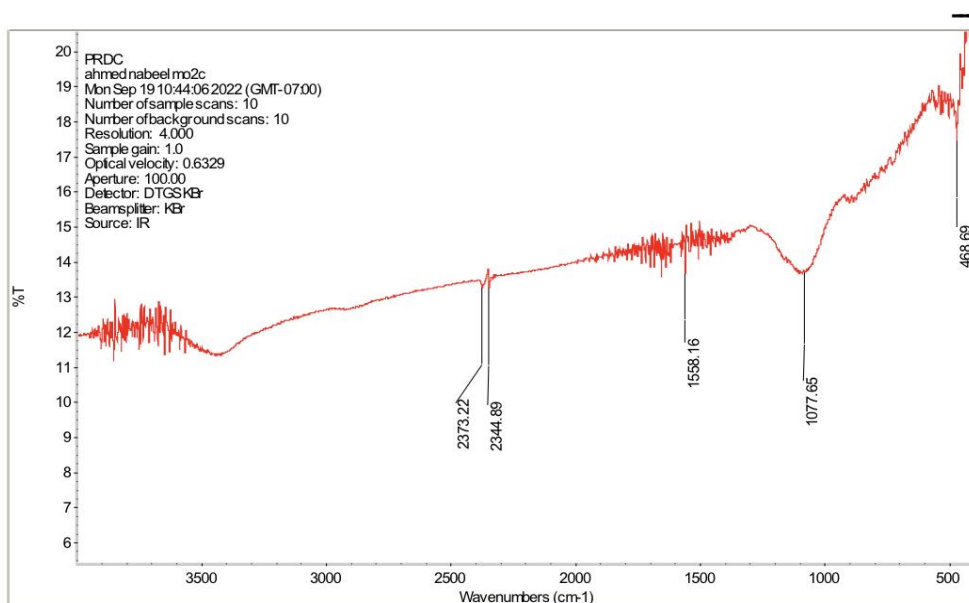


Fig. (5): FTIR for molybdenum carbide

3.2 Characterization of $\text{Mo}_2\text{C}/\text{PtHY-Zeolite}$

1. XRD

X-Ray crystallographic analysis for $\text{Mo}_2\text{C}/\text{PtHY-Zeolite}$ is summited in Figure (6) There are molybdenum indexed peaks in $2\theta = 11.8, 15.7, 20.5, 23.6, 27, 32.4, 43.1, 57.3$ showing a high level of crystallization for the band of 2θ from 10° to 60° for the produced substance on the XRD analysis. By using Scherrer's equation the average crystal size is 20.77 nm .

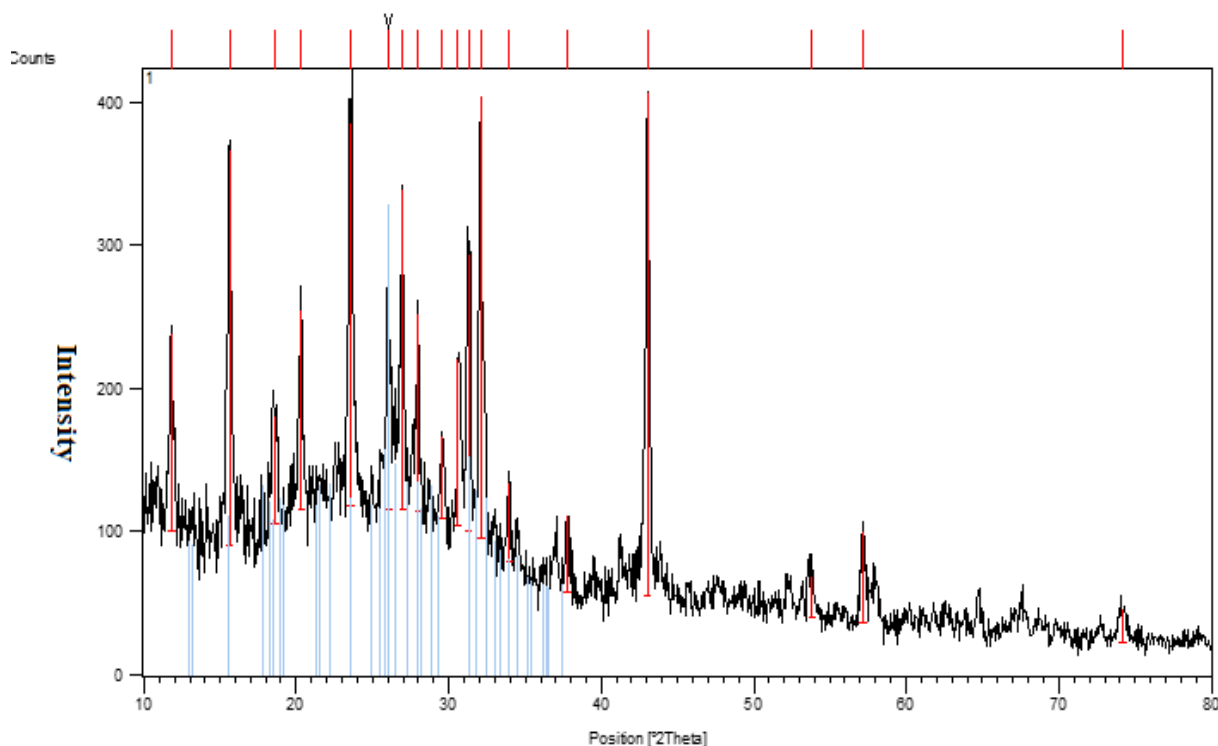


Fig. (6): XRD for MO₂C/PtHY Zeolite

2. BET surface area and Bore volume analysis

The synthesized sample Mo₂C.Pt/HY-Zeolite has an overall BET surface area of 724.55 m²/g. larger surface area means a larger pore volume which makes the catalyst more active when using it for its purpose.

3. A thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical method that analyzes the weight change that happens when sample is heated at a constant rate in order to test a material's thermal stability and the percentage of volatile components. Figure (7) shows the TGA for the prepared sample. The test shows a weight loss of 10.21% from the sample at a temperature range of 130-900 °C. From the point at 130 C to the point at 400 C the mass loss is high around 9% of the substance this is because the water evaporation as a result of rise the temperature.

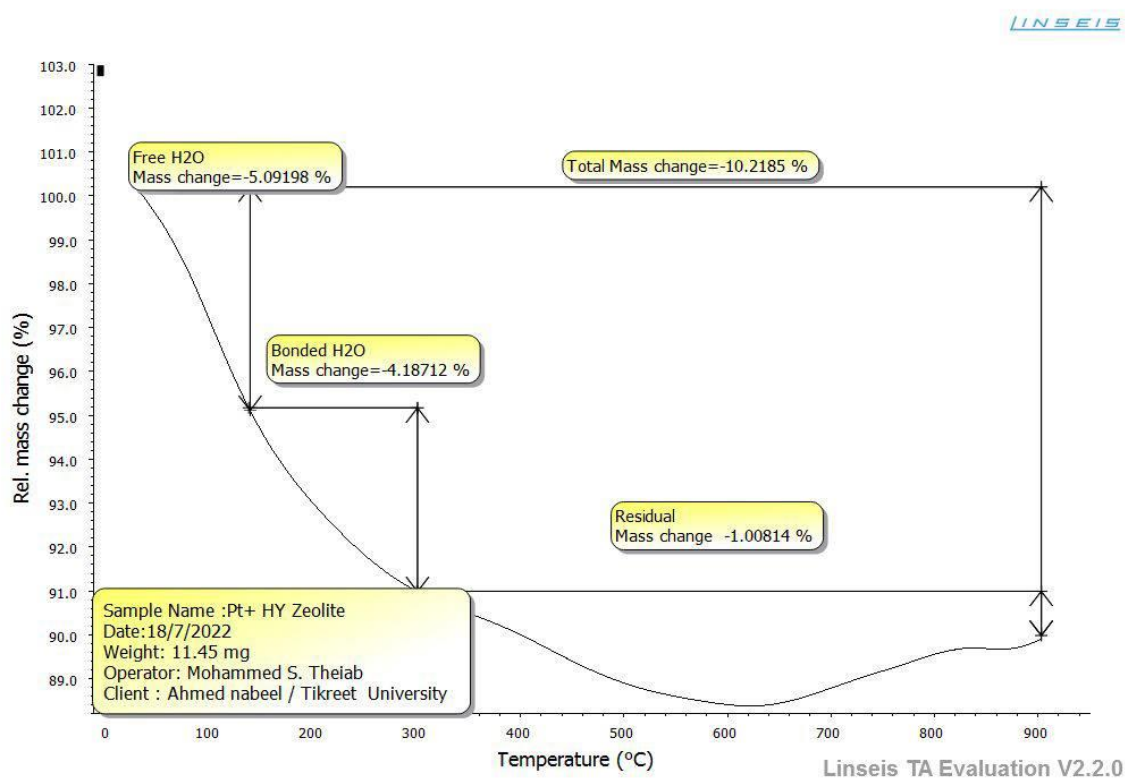


Fig. (7): TGA for Mo₂C/PtHY-Zeolite

4. Fourier transform infrared spectroscopy FTIR

The FT-IR spectra of the produced Mo₂C/PtHY Zeolite is represented in Figure (8). The IR band 2344 cm⁻¹ is caused by the stretching vibration of OH molecules. then, the IR band at 1633 cm⁻¹ is caused by the molecules' bending vibration. The band at 1057 cm⁻¹ is due to the C-C bond's symmetric stretching vibration. The detected band at 795 cm⁻¹ is due to the bond's bending vibration.

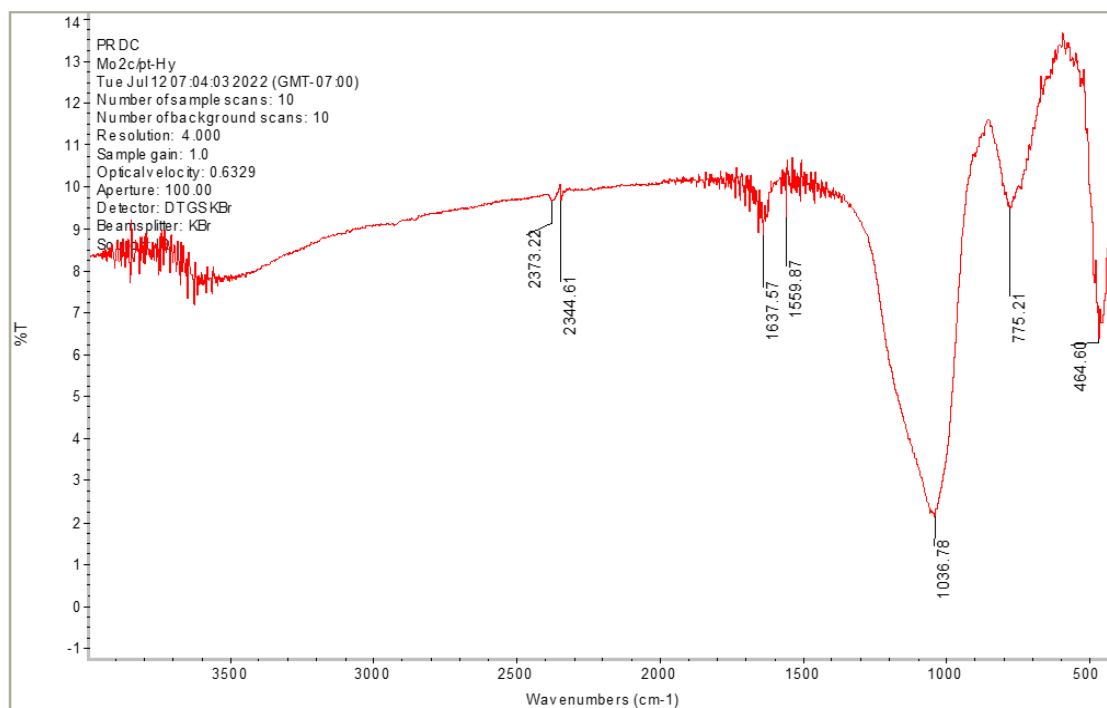


Fig. (8): FTIR Test for Mo₂C/PtHY Zeolite

3.3 Characterization of Mo₂C/CePtY

1. XRD

The X-ray diffractogram pattern of a sample of Mo₂C/CePtY is displayed in Figure (9). There is molybdenum indexed peaks in $2\theta=10.33, 12.18, 15.9, 18.9, 20.55, 23.04, 27.3, 31.7, 38.2$; showing a high level of crystallization for the band of 2θ from 10° to 40° . From XRD data and Scherrer's equation, the average crystal size for Mo₂C/CePtY is 40.43nm.

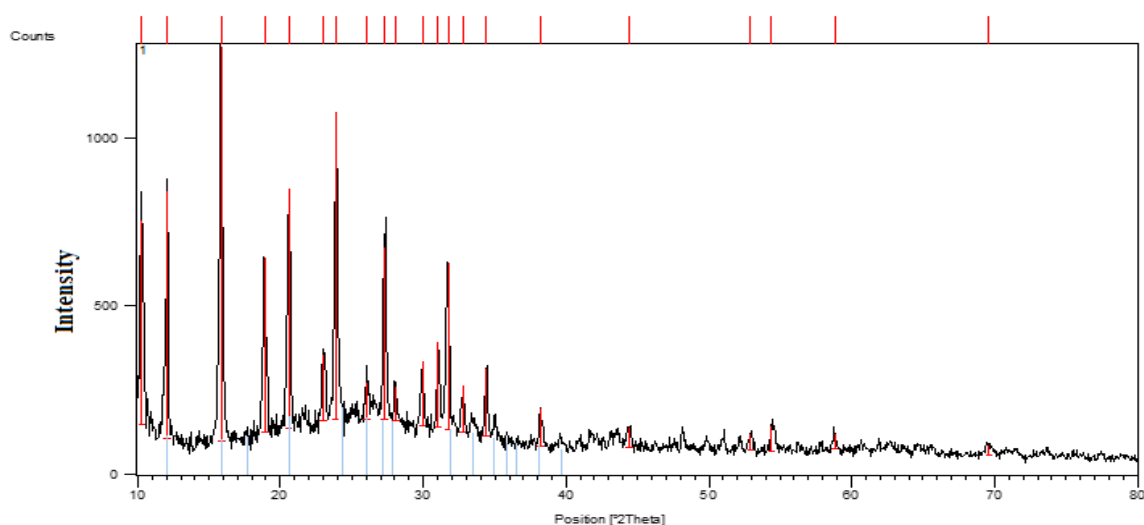


Fig. (9): XRD for Mo₂C/CePtY

2. BET surface area and Bore volume analysis

The synthesized sample of Mo₂C/CePtY has an overall BET surface area of 718.113 m²/g.

3. A thermogravimetric analysis (TGA)

TGA test depicted in Figure (10), The test shows a weight loss of 4.64504% from the sample at a temperature range of 130-900 °C. There is a large mass loss due to evaporate the molecules of water from the catalyst during the rise of temperature. The point between 300- 900 °C is a little mass loss because the substance is stable.

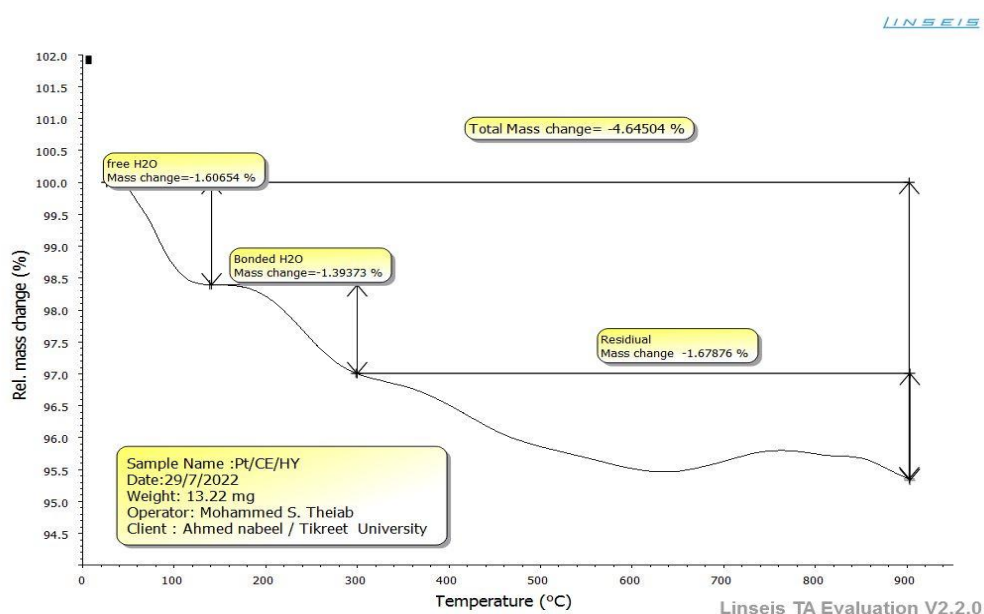


Fig. (10): A thermogravimetric analysis (TGA) for Mo₂C/CePtY

4. Fourier transform infrared spectroscopy FTIR

FTIR test represents in figure (11), The IR band 2345 is due to the stretching vibration of OH molecules. then, the IR band at 1635-1557 is caused by the molecules' bending vibration of COO molecules. The band at 1036 is due to the C_O bond's symmetric stretching vibration. Finally, the band at 914 is due to the carbon double bound CH=CH₂.

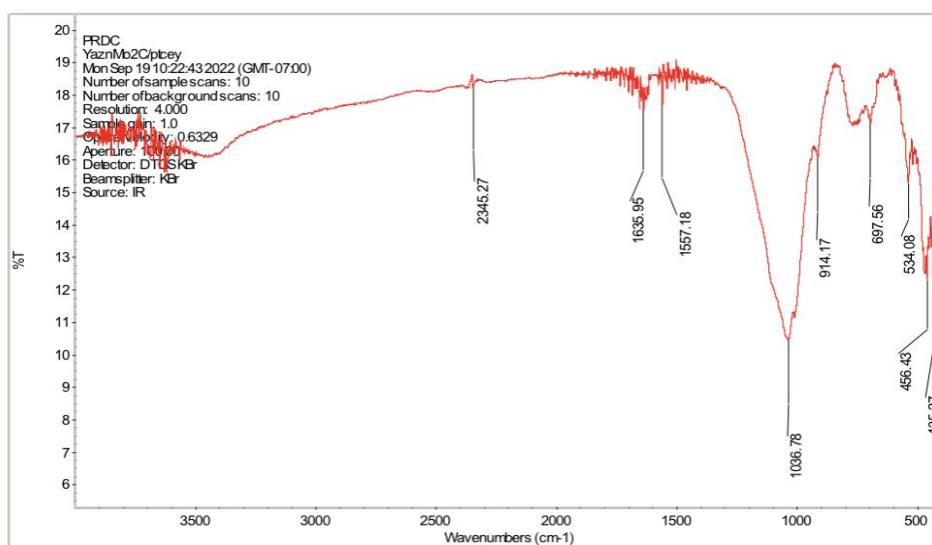


Fig. (11): FTIR for Mo₂C/CePtY

4. Conclusions:

In this study, two catalysts were synthesized, Mo₂C/PtHY and Mo₂C/CePtY. Both substances were completely tested to know their properties as shown earlier.

After synthesizing molybdenum carbide at three different temperatures the best characteristics were obtained at 900°C so it was used to prepare the two catalysts.

For the Mo₂C/PtHY zeolite and Mo₂C/CePtY, the BET surface area was 724.55 m²/g and 734.55 m²/g respectively, the large surface area of these two catalysts is due to the large surface area of the molybdenum carbide that used to produce these catalysts. The Mo₂C/PtHY zeolite's XRD pattern revealed that it had the same crystal phase structure as Zeolite Y. The Scherrer equation suggests that the average crystal size is 20.77 nm, while the crystal size of Mo₂C/CePtY is 40.43nm. A thermogravimetric analysis (TGA) for the Mo₂C/PtHY shows that the weight loss from the sample from 130-900 C is 10.21%, while for Mo₂C/CePtY is 4.64%.

References:

- [1] J. L. Hodala, S. Kotni, R. B., and B. Chelliahn, “Metal carbide as a potential non noble metal catalyst for naphtha reforming”, *Fuel*, vol. 288, Mar. 2021. <https://doi.org/10.1016/j.fuel.2020.119610>.
- [2] H. H. Hwu and J. G. Chen, “Surface Chemistry of Transition Metal Carbides”, *Chem Rev*, vol. 105, no. 1, pp. 185–212, Jan. 2005, doi: <https://doi.org/10.1021/cr0204606>.
- [3] S. Li, G. Zhang, J. Wang, J. Liu, and Y. Lv, “Enhanced activity of Co catalysts supported on tungsten carbide-activated carbon for CO₂ reforming of CH₄ to produce syngas”, *International Journal of Hydrogen Energy*, vol. 46, no. 56, pp. 28613–28625, 2021. <https://doi.org/10.1016/j.ijhydene.2021.06.085>
- [4] L. I. Johansson, “Electronic and structural properties of transition-metal carbide and nitride surfaces”, *Surface Science Reports*, vol. 21, no. 5, pp. 177–250, 1995, doi: [https://doi.org/10.1016/0167-5729\(94\)00005-0](https://doi.org/10.1016/0167-5729(94)00005-0)
- [5] E. F. Mai, M. A. Machado, T. E. Davies, J. A. Lopez-Sanchez, and V. Teixeira da Silva, “Molybdenum carbide nanoparticles within carbon nanotubes as superior catalysts for γ -valerolactone production via levulinic acid hydrogenation”, *Green Chemistry*, vol. 16, no. 9, pp. 4092–4097, 2014, doi: <https://doi.org/10.1039/C4GC00920G>.
- [6] A. Kumar and A. Bhan, “Oxygen content as a variable to control product selectivity in hydrodeoxygenation reactions on molybdenum carbide catalysts”, *Chem Eng Sci*, vol. 197, pp. 371–378, 2019, doi: <https://doi.org/10.1016/j.ces.2018.12.027>.
- [7] C. Wan, Y. N. Regmi, and B. M. Leonard, “Multiple Phases of Molybdenum Carbide as Electrocatalysts for the Hydrogen Evolution Reaction”, *Angewandte Chemie International Edition*, vol. 53, no. 25, pp. 6407–6410, Jun. 2014, doi: <https://doi.org/10.1002/anie.201402998>.
- [8] A. Kumar and A. Bhan, “Oxygen content as a variable to control product selectivity in hydrodeoxygenation reactions on molybdenum carbide catalysts”, *Chem Eng Sci*, vol. 197, pp. 371–378, 2019, doi: <https://doi.org/10.1016/j.ces.2018.12.027>.
- [9] A. bin Yousaf, F. Kveton, A. Blsakova, A. Popelka, J. Tkac, and P. Kasak, “Electrochemical surface activation of commercial tungsten carbide for enhanced electrocatalytic hydrogen

- evolution and methanol oxidation reactions,” *Journal of Electroanalytical Chemistry*, vol. 919, p. 116525, 2022. <https://doi.org/10.1016/j.jelechem.2022.116525>
- [10] M. Wu, X. Lin, A. Hagfeldt, and T. Ma, “Low-cost molybdenum carbide and tungsten carbide counter electrodes for dye-sensitized solar cells”, *Angewandte Chemie*, vol. 50, no. 15, pp. 3520-3524, 2011. <https://doi.org/10.1002/anie.201006635>
- [11] X. Chen *et al.*, “A novel catalyst for hydrazine decomposition: molybdenum carbide supported on γ -Al₂O₃”, *Chemical communications*, no. 3, pp. 288–289, 2002. <https://doi.org/10.1039/B109400A>
- [12] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, Y. Shu, A. L. Stottlemyer, and J. G. Chen, “Catalytic conversion of cellulose into ethylene glycol over supported carbide catalysts”, *Catal Today*, vol. 147, no. 2, pp. 77–85, 2009. <https://doi.org/10.1016/j.cattod.2009.03.012>
- [13] S. Li, J. Wang, G. Zhang, J. Liu, Y. Lv, and Y. Zhang, “Highly stable activity of cobalt based catalysts with tungsten carbide-activated carbon support for dry reforming of methane: Role of tungsten carbide”, *Fuel*, vol. 311, p. 122512, 2022. <https://doi.org/10.1016/j.fuel.2021.122512>
- [14] J. Han, J. Duan, P. Chen, H. Lou, and X. Zheng, “Molybdenum carbide-catalyzed conversion of renewable oils into diesel-like hydrocarbons”, *Adv Synth Catal*, vol. 353, no. 14-15, pp. 2577–2583, 2011. <https://doi.org/10.1002/adsc.201100217>
- [15] Y. Qin *et al.*, “Carbon nanofibers supported molybdenum carbide catalysts for hydrodeoxygenation of vegetable oils”, *RSC Adv*, vol. 3, no. 38, pp. 17485–17491, 2013. <https://doi.org/10.1039/C3RA42434K>
- [16] N. S. Ahmedzeki, and B. A. R. Al-Tabbakh, “Catalytic Reforming of Naphtha Using Novel Prepared Pt-Ti / HY Zeolite”, *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 17, no. 3, pp. 45-56, 2016. <https://doi.org/10.31699/IJCPE.2016.3.4>
- [17] J. Yu, B. Luo, Y. Wang, S. Wang, K. Wu, C. Liu, S. Chu, and H. Zhang “An efficient way to synthesize biomass-based molybdenum carbide catalyst via pyrolysis carbonization and its application for lignin catalytic pyrolysis”, *Bioresour Technol*, vol. 346, p. 126640, 2022. <https://doi.org/10.1016/j.biortech.2021.126640>