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MODIFICATION OF ZEOLITE-Y CATALYST BY ADDITION OF SELECTED TRANSITION METAL IONS (ZN &CU IONS)

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ABSTRACT:

Zeolite is a microporous nanomaterial with alumina and silicate structure which can be used to crack heavy petroleum fraction to yield lighter components. Recent studies suggest that zeolite can be used for sugar conversion to fuel and value-added chemicals with proper modification. In this study, fresh zeolite -y catalyst was subjected to initial characterization, Brunauser Emmett Teller (BET), X-Ray Diffractometer (XRD), X-Ray Flourescence (XRF) and Scanning Electron Microscope (SEM) and modified. 50ml of prepared standard solution of zinc and copper chloride each was added to 5g of fresh zeolite catalyst and mixed thoroughly for 1 hour at room temperature. The mixture was dried at 110 ^{0}C for 24 hours using dry oven. The crystalline solid obtained was calcined at 500 ^{0}C for 2 hours in a muffle furnace. The modified catalyst was finally characterized (BET, XRD, XRF and SEM) and the results obtained were compared with the fresh catalyst characterized results. BET results shows that the pore volume, pore diameter and surface area of the modified catalyst increase from 0.309cc/g, 2.105nm, and 627.998m2/g to 0.365cc/g, 2.446nm and 746.062m2/g respectively. Similarly, from the XRD result, the modified catalyst has all the crystalline peaks at Bragg angle (2θ) present in the fresh catalyst with additional peaks formed. The additional crystalline peaks formed show the increase in mechanical strength of the modified catalyst. The SEM results show the change in surface texture of the fresh catalyst from smooth and uniform to rough and agglomerated.

Keywords: Zeolite, Catalyst, Transition metals. Modification, Crude, ions

3. 0 INTRODUCTION

Catalyst is any substance that increases the rate of a reaction without itself being consumed. Most solid catalyst are metals or the oxides, sulfides, and halides of metallic elements and of semi-metallic elements, boron, aluminum, and silicon. Gaseous and liquid catalyst are commonly used in their pure form or in combination with suitable carriers or solvents. In general, catalytic action is a chemical reaction between the catalyst and a reactant, forming chemical intermediates that are

able to react more readily with each other or with another reactant to form the desired end product. During the reaction of the chemical intermediates and the other reactants, the catalyst is regenerated.

Fluid Catalytic Cracking (FCC) is the conversion process used in petroleum refineries to convert the high-boiling point, high-molecular weight hydrocarbon fractions of petroleum (crude oils) into gasoline, olefin gases, and other petroleum products. The cracking of petroleum hydrocarbons was originally done by thermal cracking, now almost replaced by catalytic cracking, which yields greater volumes of high -octane rating gasoline; and produces by-product gases, with more carbon double bonds (i.e. olefins), that are of greater economic value than the gases produced by thermal cracking.

The feedstock to the FCC conversion process usually is heavy gas oil (HGO), which is that portion of the petroleum (crude oil) that has an initial boiling-point temperature of 340 °C (644 °F) or higher, at atmospheric pressure, and that has an average molecular weight that ranges from about 200 to 600 or higher; heavy gas oil also is known as “heavy vacuum gas oil” (HVGO). In the fluid catalytic cracking process, the HGO feedstock is heated to a high temperature and to a moderate pressure, and then is placed in contact with a hot, powdered catalyst, which breaks the long-chain molecules of the high-boiling-point hydrocarbon liquids into short-chain molecules, which then are collected as a vapor.

Zeolites represent a revolution of crystalline porous materials. They are an important group of heterogeneous catalysts with large-scale applications in the petroleum industry and an increasing application potential in environmental catalysis. Zeolites are crystalline alumina silicates with 3D four-connected frameworks built by corner sharing SiO_4 and AlO_4 units and a Si/Al ratio greater than one. Other atoms with tetrahedral coordination such as Ge, B, and Ti can also be introduced into the framework and enrich the zeolite family (Foster et al., 2012).

2.0 METHODOLOGY

Materials

The following materials and reagents were used for this research; fresh zeolite catalyst, Zinc Chloride, Copper II chloride, Hydrochloride acid and distilled water. The materials were sourced from school laboratory and open market.

The equipment used for the research includes weighing balance, magnetic stiller, oven ,beakers, muffle furnace, measuring cylinder.

Methodology

Fresh catalyst (Zeolite Y) was obtained from Kaduna Refining and Petrochemical Company (KRPC), Kaduna state in Nigeria. The zeolite catalyst was subjected to initial characterization

(**SEM, BET, XRD** and **XRF**) to ascertain its original nature in Ahmadu Bello University (ABU) multi-user laboratory before the modification process was carried out in the laboratory .

Preparation of Standard Solution of Zinc Chloride

13.63g of granulated zinc chloride was dissolved in a minimum amount of 0.1M (100 ml) HCL. 700 ml of purified water (distilled water) was added, mixed and allow to cool to room temperature. The volume was made up to 1000 ml with purified water. The solution was mixed thoroughly.

Preparation of Standard Solution of Copper Chloride

1.965g of cupric chloride accurately weighed, was dissolved in sufficient 0.1M (100 ml) of HCL. The volume was made up to 1000 ml with distilled water and mixed thoroughly.

Mixing

5g of the zeolite catalyst was introduced into a 500 ml beaker. 50 ml of zinc chloride and 50 ml of cupper chloride standard solution were added to the zeolite in the beaker. The solution was subjected to magnetic stirrer for mixing in order to achieve homogeneity. The stirring was done for 2 hours at room temperature (25 ^{o}C)

Drying

In order to remove the liquid solution, present in the mixture, the mixture was dried to a crystalline solid in a dry oven at 110 ^{o}C for 24 hours.

Calcination

The dried crystalline zeolite was calcined in a muffle furnace at a temperature of 500 ^{o}C for 2 hours. Finally, the calcined zeolite was characterized (i.e. **SEM, BET, XRD and XRF).**

3. 0 Discussion of Results

XRD Analysis:

Quantitative analysis report

General information

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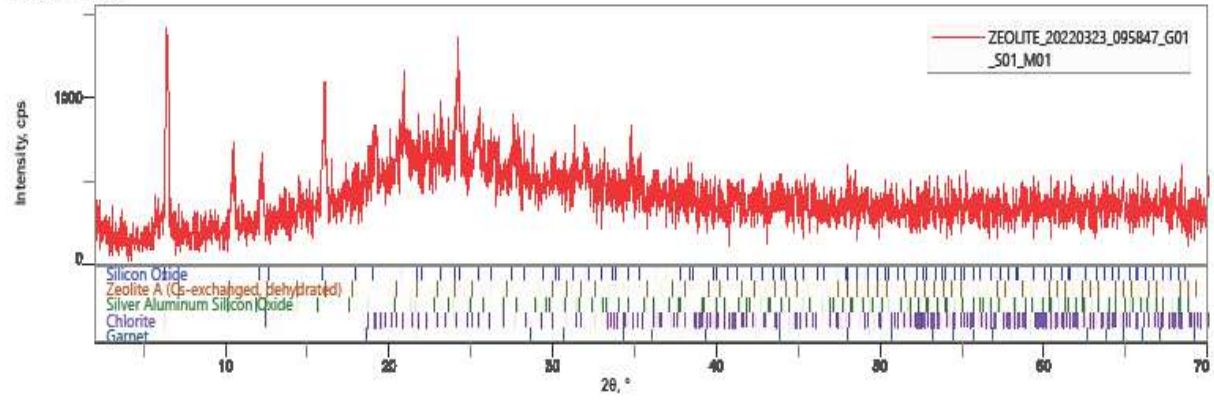
Multiple Profile



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Quantitative analysis report

General information

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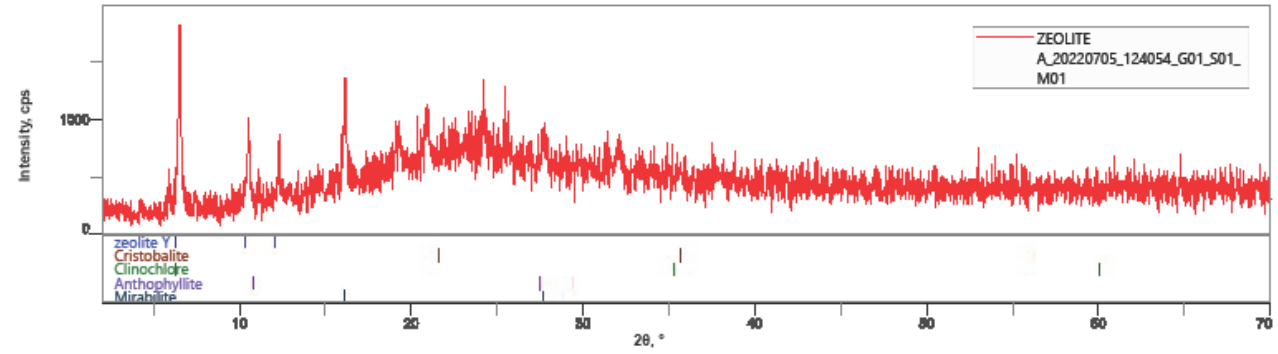


Quantitative analysis report (Solution) Page 1 of 2

From Figure 4.1 above, the XRD pattern shows that, the crystallinity of the fresh catalyst at 2θ = 7^o, 10.2^o, 12^o, 15^o, 22^o, 25^o, 31^o and 35^o. From FIG. (4.2), the modified catalyst has all the crystalline peaks present in the fresh catalyst with additional peaks formed. The additional peaks formed are; 2θ = 16^o, 19^o, 27^o, 28.5^o and 33^o. this implies that the more active crystalline peaks are formed, the more the mechanical strength or activity increases and vice versa. This follows the trend as reported by Nwosibe *et al*. (2018).

XRF Analysis:

XRF Results for Test Sample of Fresh and Modified Catalyst.

Oxides	**Fresh Catalyst**		**Modified Catalyst**	
	Concentration	**Mole (%)**	**Concentration**	**Mole (%)**
SiO_2	**44.226**	**54.398**	**51.310**	**61.60**

Al_2O_3	**32.996**	**23.347**	**41.303**	**29.938**
ZnO	**0.011**	**0.010**	**6.425**	**5.695**
TiO_2	**2.700**	**2.498**	**3.397**	**3.069**
Cl	**0.608**	**1.267**	**2.064**	**4.201**
Fe_2O_3	**1.073**	**0.498**	**1.503**	**0.679**
CuO	**0.038**	**0.035**	**0.614**	**0.557**
V_2O_5	**0.358**	**0.145**	**0.358**	**0.142**
Cr_2O_3	**0.185**	**0.090**	**0.266**	**0.126**
NiO	**0.023**	**0.023**	**0.062**	**0.060**
CaO	**0.090**	**0.118**	**0.152**	**0.196**

From Table 3.1 above, the concentration and mole percent of the key oxides such as; SiO_2, Al_2O_3, ZnO, etc. decreased in the fresh catalyst. It can be seen from the above that, in the modified catalyst, the oxides increased in both concentration and weight percent. This is in line with what was reported by Foster et al. (2012).

BET Analysis:

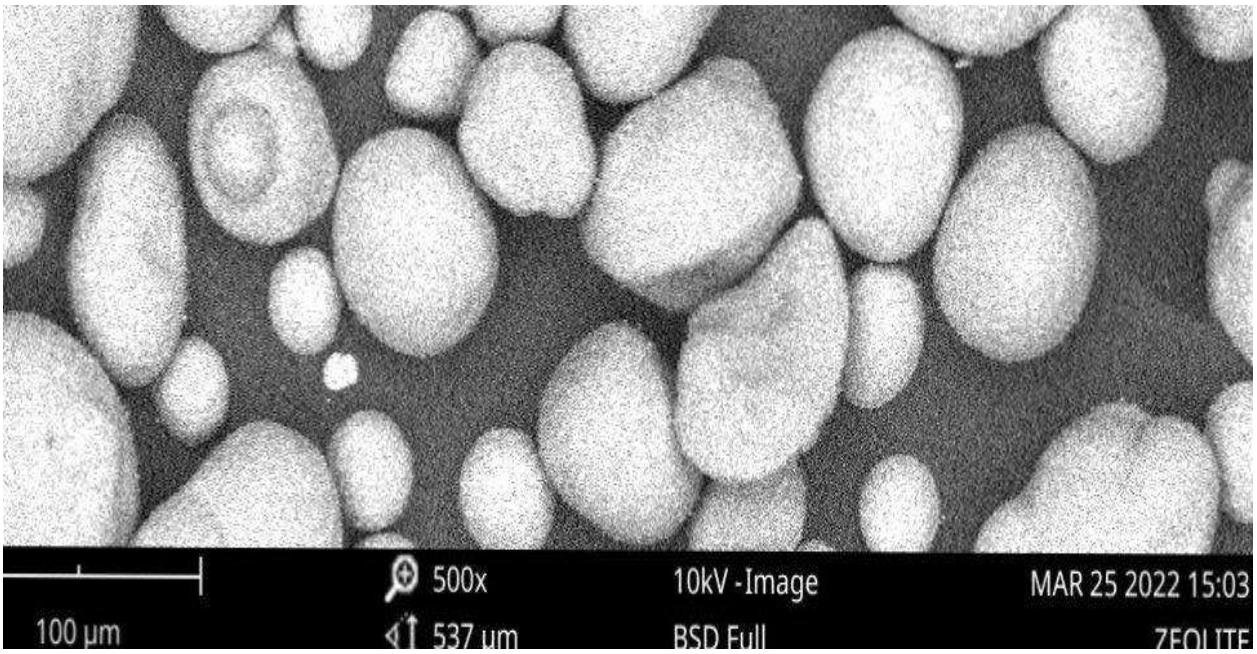
Table 3.2: BET Surface Area, Pore Volume and Pore Diameter for Fresh and Modified Zeolite Catalyst.

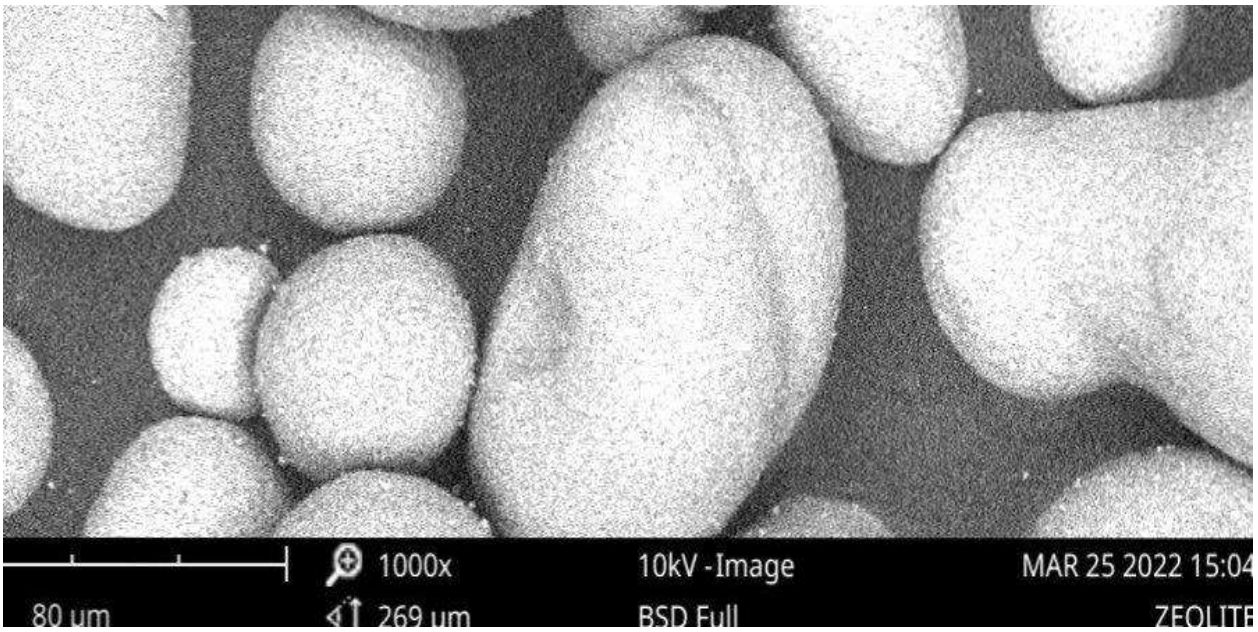
Sample	Surface Area (M2/G)	Pore Volume (Cc/G Or Cm3/G)	Pore Diameter (Nm)

Fresh catalyst	**627.998**	**0.309**	**2.105**
Modified catalyst	**746.062**	**0.365**	**2.446**

The surface area, pore volume and pore diameter of the fresh catalyst were determined by BJH Adsorption Method and the results were summarized in Table 3.2 above. As shown in Table 3.2, the surface area, pore volume and pore diameter of the modified catalyst increased after the addition of the additives, especially zinc and copper chloride. This follows the trend as reported by Paasikollio et al. (2014).

SEM Analysis:

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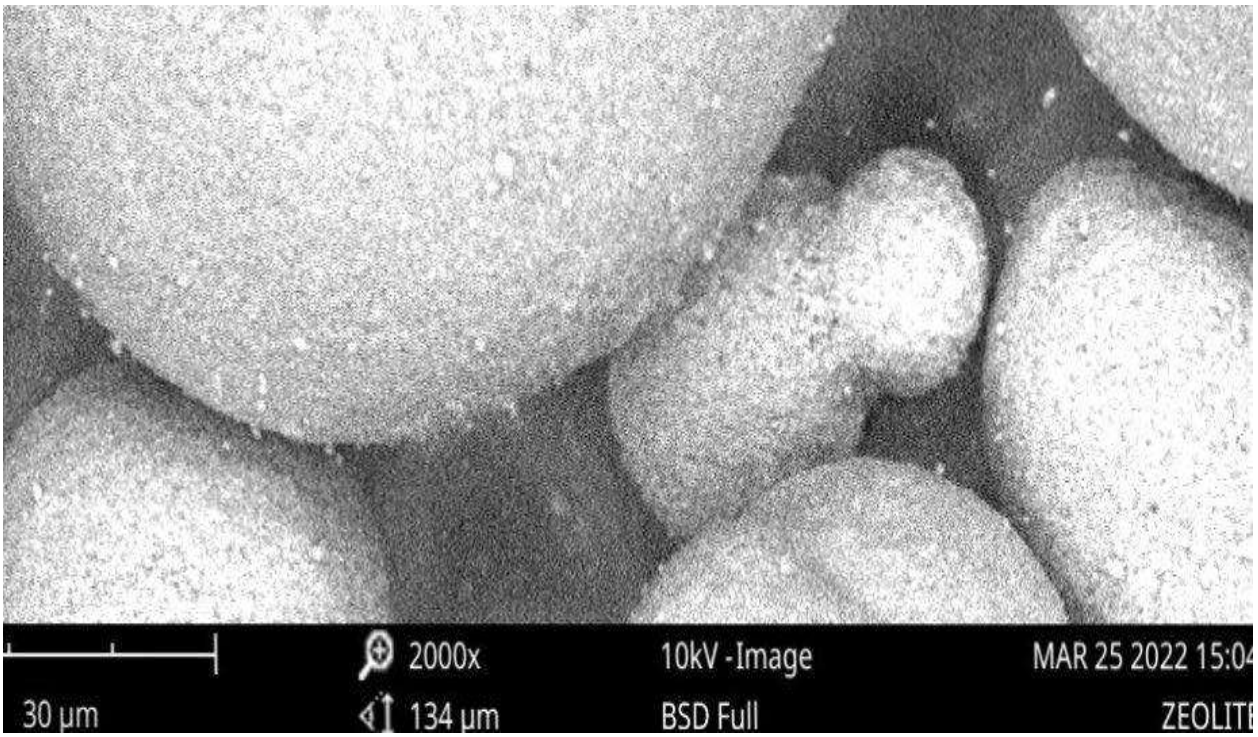
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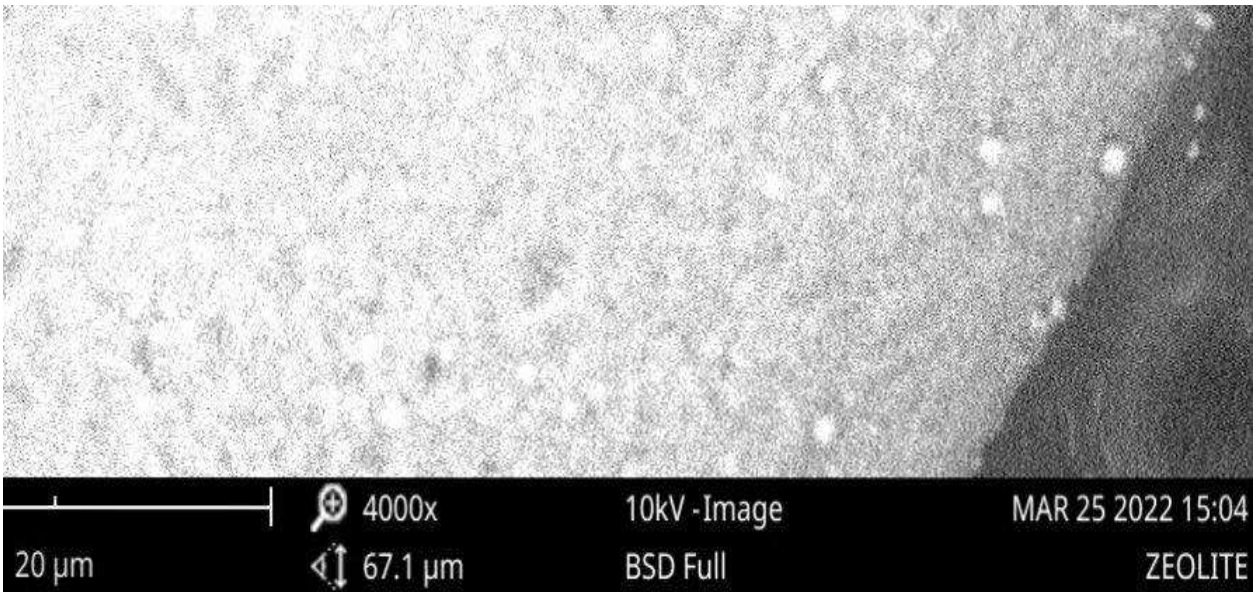
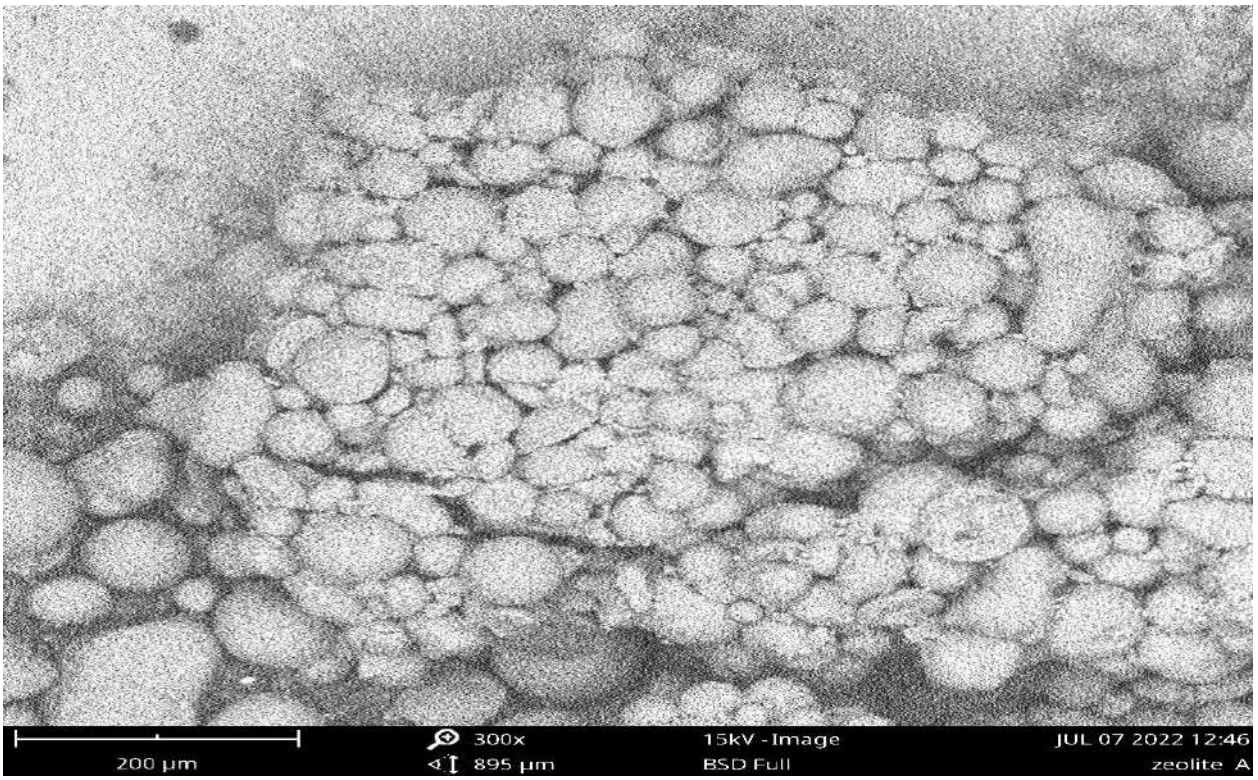
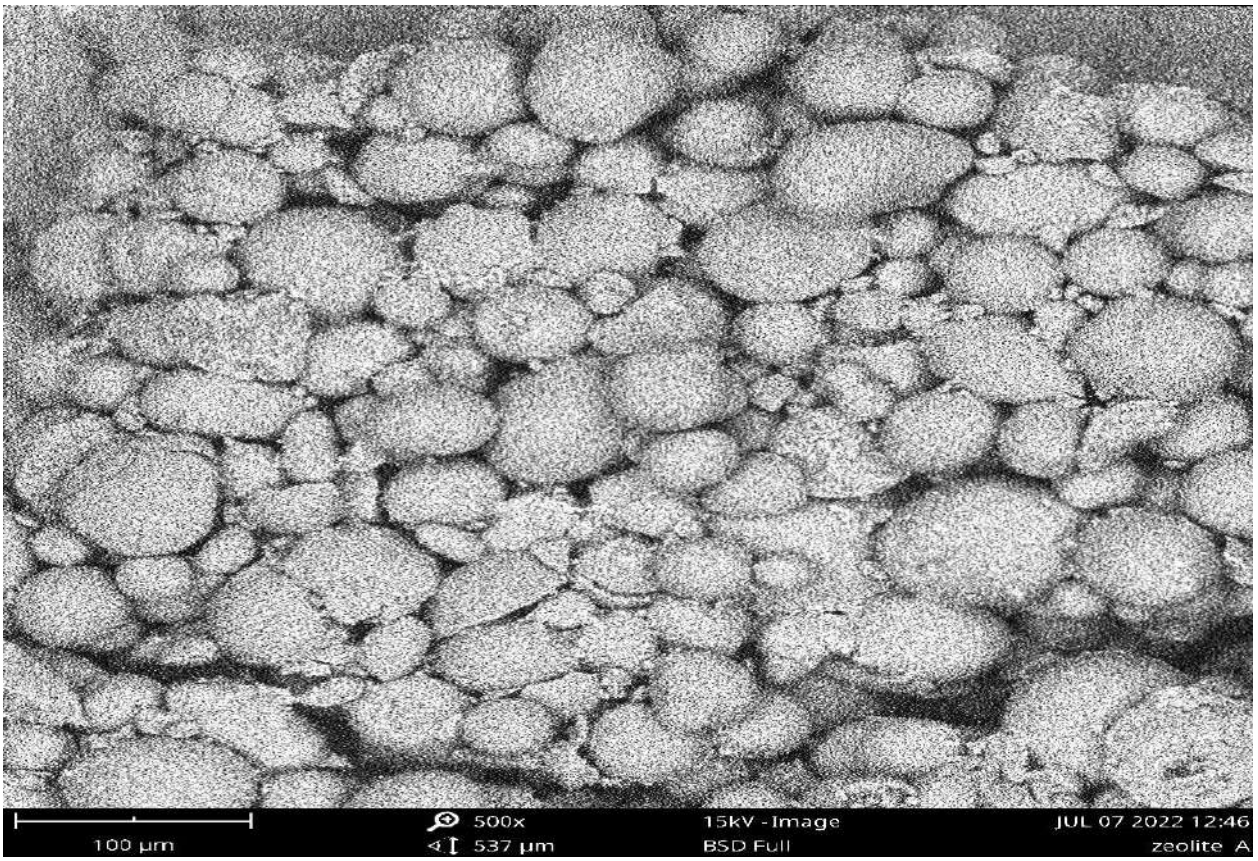


Figure 3: SEM Images of Fresh Catalyst

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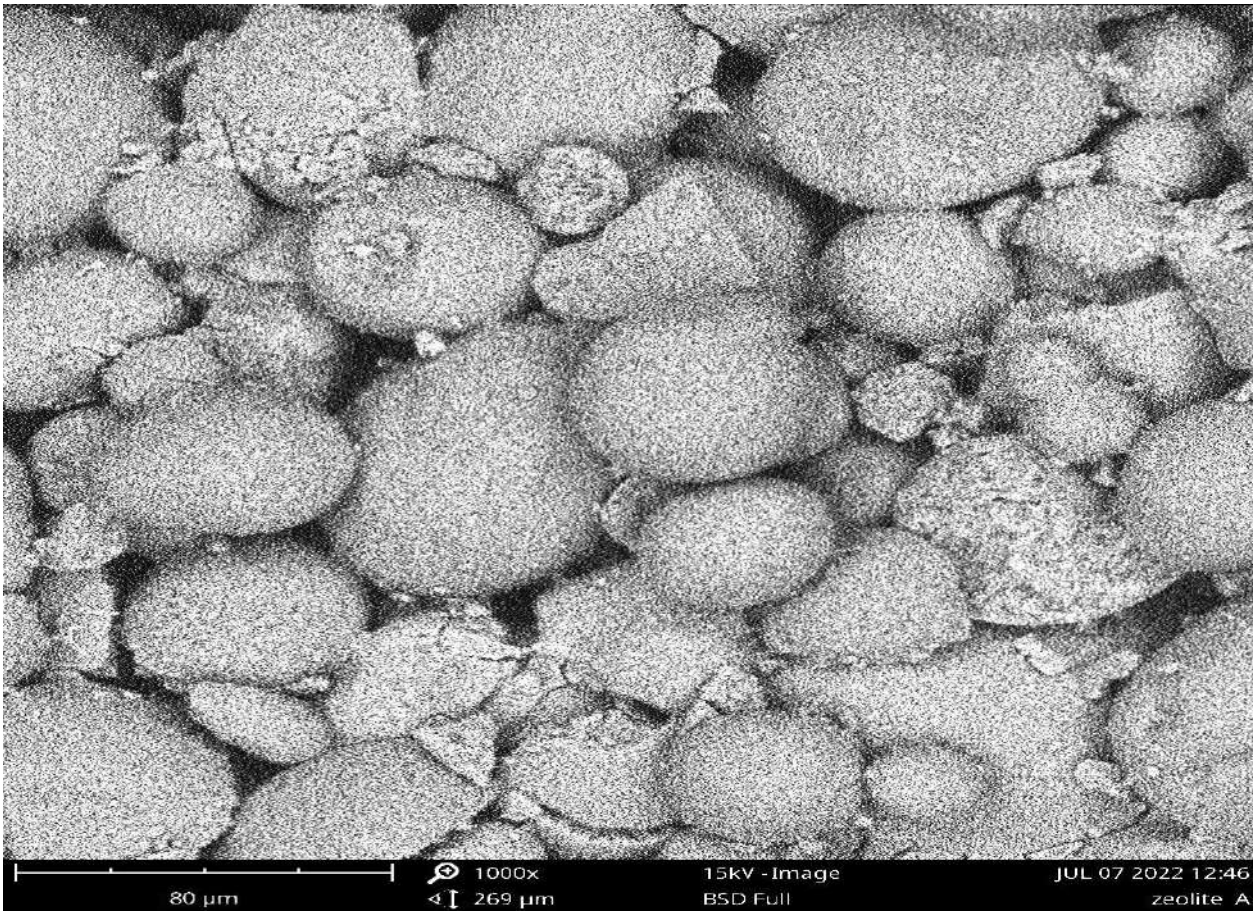
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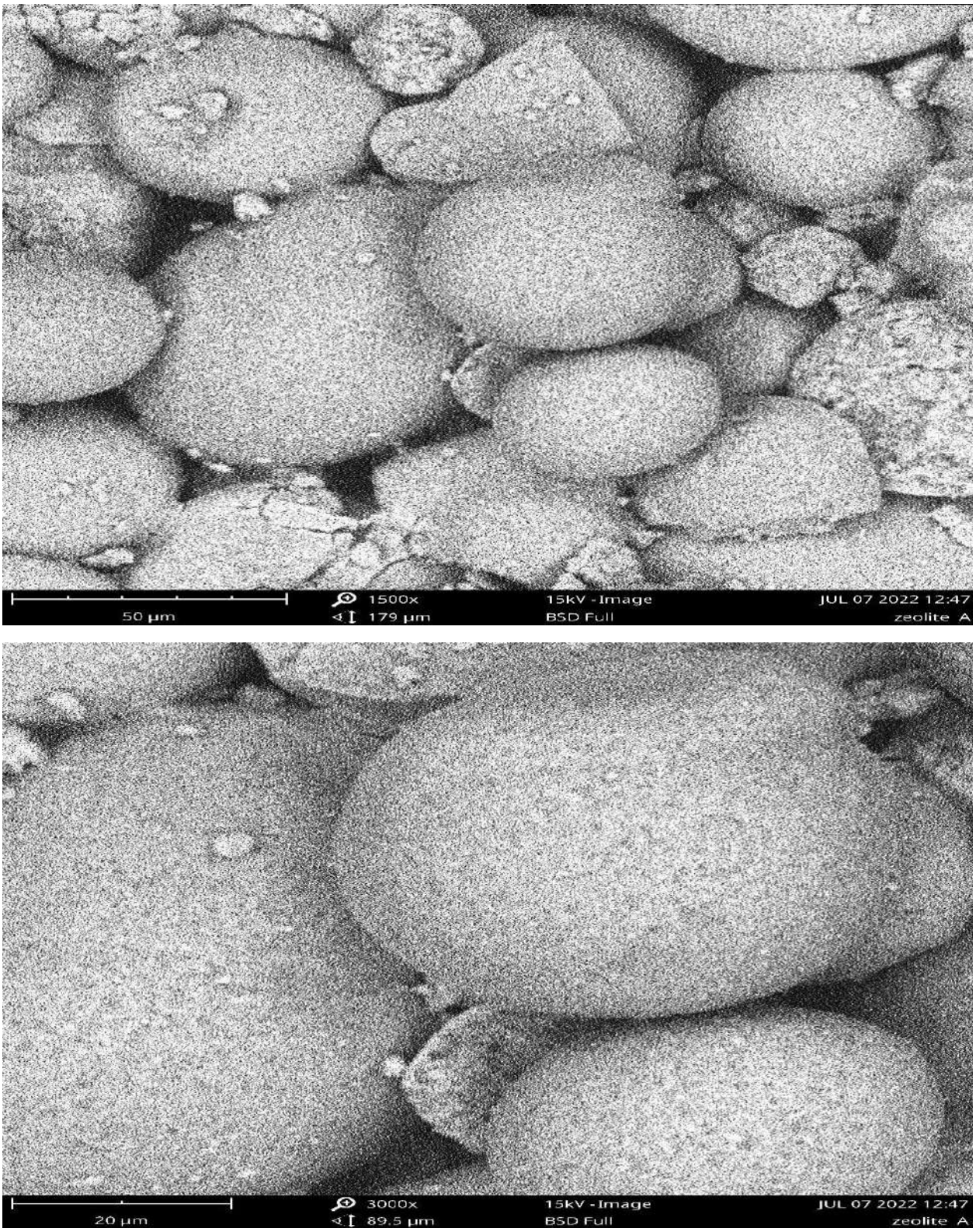

Figure 3: SEM Images of Modified Catalyst.

Scanning Electron Microscopy (SEM):

In order to observe the changes of the surface morphology and the amount of the surface elements of the fresh and modified catalyst, SEM experiment was conducted and the results are shown in figure 4.3 and 4.4 respectively. As illustrated in figure 4.3, the surfaces of the fresh catalyst are

smooth and uniform. While after the modification with ZnO and CuO in figure 4.4, a significant agglomeration and sulfates deposited on the surface could be observed. This implies that the catalyst modified by ZnO and CuO could reduce the deposition of ammonium sulfate on the surface of the catalyst. This is in line with what was reported by Jin et al. (2014).

4.0 CONCLUSION

The fresh (commercial) zeolite was sourced and characterized. **XRD** pattern shows the major and minor crystalline peaks at Bragg (2θ). The concentration and weight % of the major oxides **(**SiO_2 and Al_2O_3) were determined from the **XRF** analysis. **BET** result shows the pore volume, pore diameter, and surface area of the fresh catalyst which were recorded in Table 4.2. It was observed from the **SEM** analysis conducted, the surface texture of the fresh catalyst was found smooth and uniform.

The fresh catalyst was modified by addition of a prepared standard solution of Copper and Zinc Chloride.

The modified catalyst was subjected to **BET, SEM, XRD** and **XRF** analysis. **BET** results shows that the pore volume, pore diameter and surface area of the modified catalyst increase from 0.309cc/g, 2.105nm, and 627.998m^2/g to 0.365cc/g, 2.446nm and 746.062m^2/g respectively. Similarly, from the XRD result, the modified catalyst has all the crystalline peaks at Bragg angle (2θ) present in the fresh catalyst with additional peaks formed. The additional crystalline peaks formed shows the increase in mechanical strength of the modified catalyst. The SEM results shows the change in surface texture of the fresh catalyst from smooth and uniform to rough and agglomerated.

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