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Study of the Effect of Attrition on the Properties of Catalyst Used for Industrial FCC Operation

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Abstract: *In this study, the effect of attrition on the properties of a commercial catalyst used for industrial Fluid Catalytic Cracking (FCC) process has been investigated. Catalyst loss, physicochemical, and structural properties are some of the properties which have been used to evaluate the effect of attrition on the catalyst. BET, Sieve, XRF, SEM and XRD analysis were carried out on the fresh and spent catalysts. Attrition Index, which is a measure of the resistance of these catalyst samples to attrition, was also determined. Total surface area (118 m^2/g), apparent particle size (75 μm), and compositional analysis all indicate the effect of attrition on the properties of the catalyst. The least sized particles were most attrited whereas SEM and XRD analysis showed the impact of attrition on the morphology and crystallinity of the particles. The attrition indices for the fresh and spent catalyst were found to be 58.9 and -2.50 respectively.*

Keywords*: Fluid Catalytic Cracking Unit, Catalyst Attrition, Physicochemical Properties, Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD).*

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I. Introduction

One major cause of catalyst deactivation in the FCC process is attrition. It occurs due to particle motion and inter-particle collision resulting from gas flows and the bed-to-wall impact on the process. Although these collisions are required for the efficient performance and operation of fluidized-bed reactors, the resulting attrition is a major drawback in the operation of these units. The main consequence of catalyst attrition is the generation of fines which eventually pass as dust leading to the loss of valuable catalyst materials [1, 2]. This loss has both operational and economic implications in the running of these units. Loss of catalyst particle fines increases the coarseness of the bed particle size distribution hence the need for addition of makeup catalyst in order to keep the system at a required level of fines [3, 4]. Whereas increased coarseness is undesirable, having large amount of particle fines within the system could give rise to a fluidized bed whose particle size distribution may be too fine to achieve the desired result.

Attrition could originate from the grid jet, within the fluid bed (bubble phase), and inside the cyclone. Attrition within these regions has been evaluated and models developed for them as well [4]. Attrition is time dependent with varying characteristic responses for the steady state and non-steady processes. Mathematical models have been used to describe the dependence of attrition on time [5 – 7]. While attrition rate decreases with time, specific attrition rate describes the intrinsic behavior of catalyst particles [1]. Wei et al [2] attributed reasons for catalyst losses to possible existence of catalyst attrition in all FCC units knowing that there are many channels through which attrited catalysts could be lost in the process. As much as some of these loss channels could be controlled e.g. withdrawal from the bottom of the regenerator, others like the regenerator exhaust system cannot be controlled. Catalysts leaving through these routes usually contain more microfines than those circulating within the main unit [2].

Attrition in fluidized beds could be influenced by catalyst particle properties, fluidization conditions, and bed structure parameters [1]. Catalyst particle properties include material properties, textural properties, mechanical strength, catalyst shape, particle size, surface roughness, hardness, microcracks etc. Fluidization conditions are: gas velocity, pressure, temperature, density, humidity etc., whereas fluidized bed structure parameters describe orifice number for multi-orifice distributor plates among others [5]. Particle size have been studied as a factor of attrition using a jet-cup apparatus for several FCC catalysts [8], while Chen et al [9] studied the attrition of catalyst particles in a high-velocity air-jet apparatus. Particle morphology, system composition, and operating conditions are other key factors reported to affect attrition of catalyst particles [10,

11]. Attrition modes range between abrasion and fragmentation resulting in the production of elutriable fines which do not alter the composition of the mother particle as well as particle breakage respectively [12].

Other works on catalyst attrition testing include that of Kukade et al [13] which compared attrition measurement between ASTM and Jet cup methods, Amblard et al [14] also studied attrition in a Jet cup rig whereas attrition in a Circulating Fluidized Bed (CFB) was evaluated by Thon et al [15]. Hao et al [16] studied the influence of temperature and time on the attrition mechanism. A review on nature and mechanisms including methods for its characterization, as well as the various test methods was done by Bemrose et al [17], Forzatti and Lietti [18]. The works of Meyer et al [19] and Chiranjeevi et al [20] also addressed other factors affecting catalyst attrition. Although most of these laboratory-scaled studies proffered solutions on process improvement of this unit, evaluating the effect of catalyst attrition in an industrial scaled process is necessary. Some works on catalyst attrition investigate catalyst degradation on laboratory-scale using standard test methods [1, 15, and 21]. These tests classify catalysts based on their proneness to attrition; but, however, fail to predict its impact on a large scale process and under normal operating conditions for a fluidized-bed process. The limited applicability of these predictions arise from the different stress mechanisms associated with real-time operation as against the uniform pattern assumed in these laboratory studies, hence the need for this study.

Moreover, as much as a global understanding of the attrition process is desirable, peculiarities of each unit make it unrealistic to expect a particular solution to address the challenge of catalyst attrition in all the FCC units. Considering that attrition in industrial FCC units leads to catalyst loss, it is important to analyze the extent to which the properties of the catalysts are affected in this process. Various physical, structural and chemical properties of the catalyst shall be examined to evaluate the impact of attrition on the properties of this commercial grade catalyst. This study targets an investigation on the effect of attrition on the properties of a commercial grade catalyst used in large scale fluid catalytic cracking process with a view to enhancing efficient operation of the unit.

II. Method

The methods used in this work were as follows:

2.1 Technical evaluation

Technical evaluation of the design and operation of a selected FCC unit in Nigeria (UOP technology) was done. Data from 5 continuous run operations were used to study the effect of attrition on the commercial grade catalyst under consideration. The catalyst level inside the regenerator during operation was evaluated from the pressure exerted by the catalyst at each point in time and recorded on a 6 hr interval while the amount of the makeup catalyst was deducted so as to evaluate the catalyst loss in the process.

2.2 Catalyst Characterization

The commercial grade catalyst used in this work consists mainly of Y-zeolite with an Alumina base built on Nickel support. Its length and bulk density were 3 – 6mm and 0.8g/cm^3 respectively. Other physical and chemical properties which were used to characterize the fresh and spent catalyst include: particle size, total surface area, sodium oxide and rare earth oxide content analysis. Sieves were used to evaluate the particle size of the catalyst while the catalyst morphology and its crystallinity were evaluated using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) respectively. SEM was done using a Phenom ProX model of SEM machine which rely on electric fields to create an image, hence the catalyst samples were further pulverized to avoid interference with the electric beam. Also, these samples were first coated with 5nm of gold (for conductivity) before being transferred into the column of the SEM machine with the aid of a sputter coater for analysis. The X-Ray diffraction (XRD) data were obtained with a Bragg Brentano diffractometer (Model No. D5005 Θ- :2Θ) equipped with a curved graphite crystal diffracted beam monochromator and NaI scintillation detector using CuKα radiation. The orientation effect on the crystals was suppressed using finely-ground powder. The XRD data was obtained for count time of 5s/step and with a step increment of 0.020 2 Θ. The impacts of attrition on these properties were analyzed through deductions made from the results obtained. The crystallinity was obtained using Originpro 2018 and Microsoft Excel 2013 softwares and evaluated using with Equation 1

$$\text{Crystallinity} = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks}} * 100 \quad (1)$$

III. Results and Discussion

3.1 Technical evaluation

The observations from the technical evaluation of the FCC unit is shown in Table 1

Table 1: Design and operating conditions of regenerator

		Operating Condition				
Parameter	**Design**	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**
Regenerator Dense Bed Temp (^oC)	680	681	695	723	716	710
Regenerator Pressure (KNm^{-2})	206.92	216.72	211.82	215.75	220.65	218.69
Air flowrate (KNm^3/hr)	155.7	129.72	129.87	130.04	129.99	128.08
Blower air discharge Pressure (KNm^{-2})	350.09	294.2	196.13	294.2	294.2	294.2
Air Temperature (^oC)	183.6	184	176	178	181	179
Air blower speed (krpm)	5.8	6	6	6	6	6

NB: average values for the operating data has been provided

Table 1 shows the design and operating condition of the regenerator section of the FCC unit during the period under investigation. Compared to the design values, the catalyst bed temperature of 723 ^oC for the 3rd run operation was the highest whereas the 681^oC for 1st run operation was the least and also closest to the design value which is 680 ^oC. The fluidizing air temperature for the 1st run operation was also the closest to the design value. Also, the regenerator pressure of 220.65 KNm^{-2} for the 4th run operation was the highest within this unit and could have some implications on catalyst attrition.

3.2 Catalyst loss on the system

The mass of catalyst within fluid bed was evaluated from the pressure exerted by the catalyst inside the regenerator and monitored from the control unit. The catalyst loss at each run is shown in Figures 1 to 5.

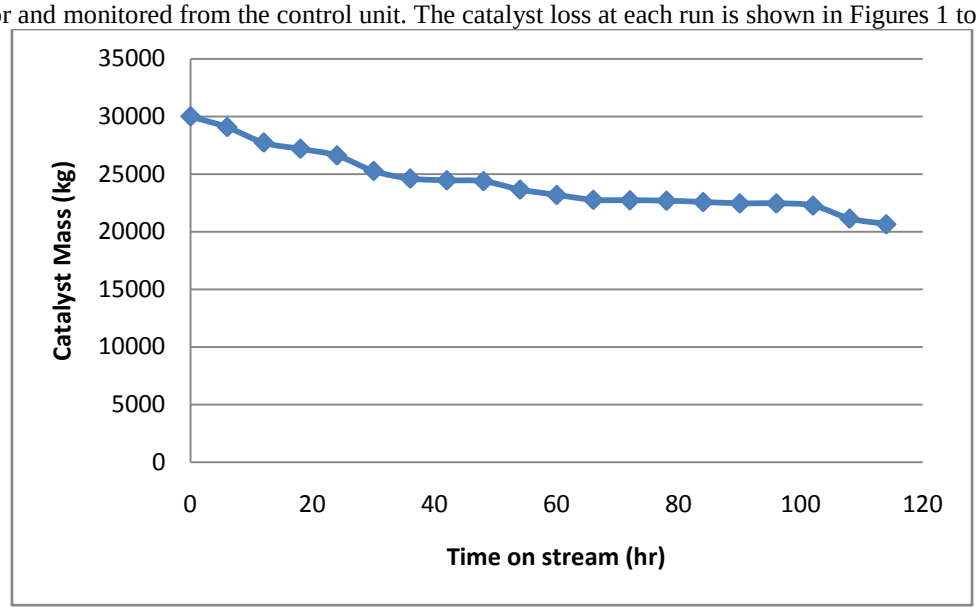


Figure 1: Catalyst Mass Vs Time for Run 1

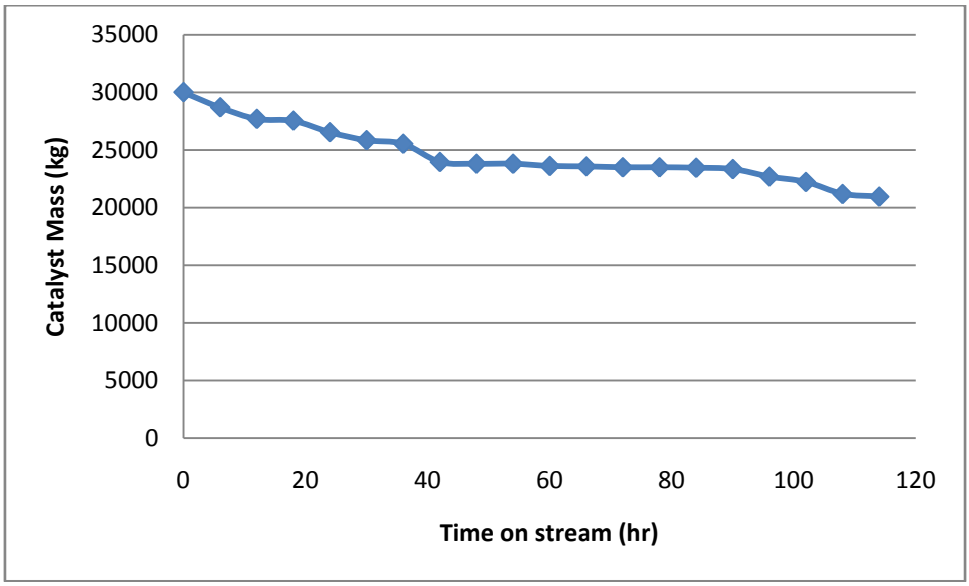


Figure 2: Catalyst Mass Vs Time for Run 2

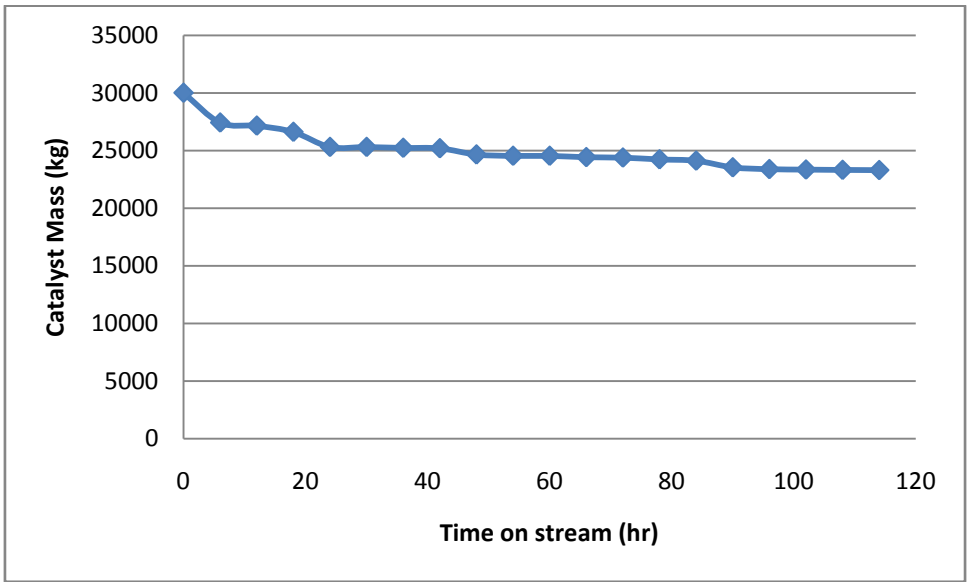


Figure 3: Catalyst Mass Vs Time for Run 3

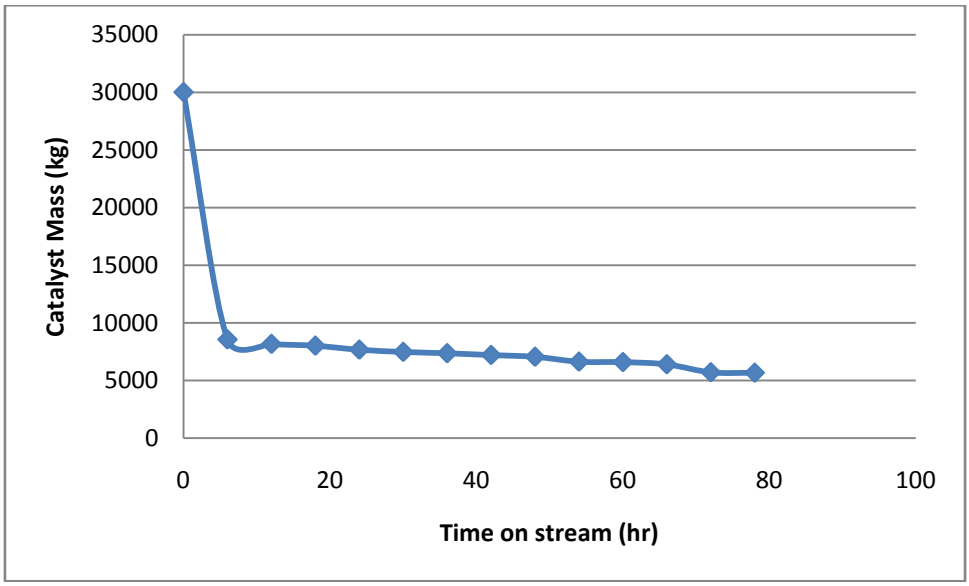


Figure 4: Catalyst Mass Vs Time for Run 4

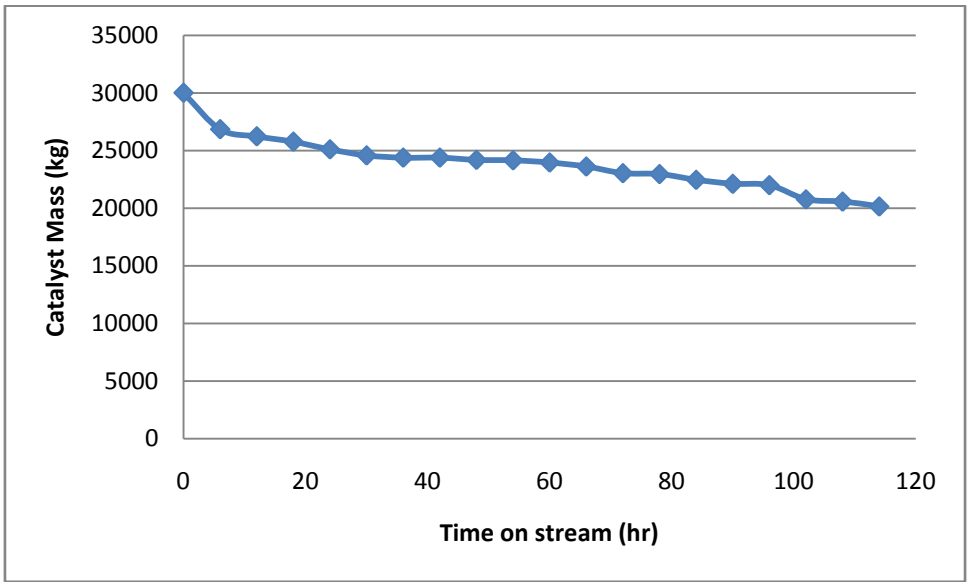


Figure 5: Catalyst Mass Vs Time for Run 5

Figures 1-5 show a general decline in the mass of the catalyst bed inside the regenerator for all the cases considered. In this study the amount of makeup catalyst ≈2700kg/day (3tons/day) was first deducted. The sharp decline observed in Figure 4 could be due to the high pressure of the 4th run operation which might have had serious consequence on catalyst loss and the attrition process or could indicate a technical fault in the unit; although a gradual decline in mass is observed in Figures 1, 2, 3 and 5. The gradual decline in the mass of the catalyst implies a steady loss of elutriable fines within this unit which Wu et al [1] had ascribed to characteristic loss of smaller fines in the catalyst bed leading to increased coarseness of the fluid bed [3]; although with continuous removal of the surface layer from the parent material, these coarse particles could undergo further attrition over time [20]. The initial sharp decline could infer the unsteady state process described by Wu et al [1]. Moreover, whereas increased pressure within the regenerator could be said to have had a significant impact on the catalyst loss and attrition process, the same cannot be said of temperature. In other words, mechanical stress rather than thermal stress could be responsible for attrition in this unit; although there is need for further research in this area.

3.2` Catalyst Characterization

Table 2: Physicochemical property analysis of the catalyst

Property	Fresh Catalyst	Spent Catalyst
Apparent Particle Size (μm)	71	75
Total Surface Area (m^2/g)	251	118
Rare Earth Oxide (wt%)	1.9	1.6
Sodium Oxide (wt%)	0.3	0.2

Note: values for the spent catalyst were the average from 5 run operations

Table 2 shows that there were variations in the properties of the fresh and spent catalysts. Increase in the apparent particle size of the catalyst from 71 μm for the fresh catalyst to 75 μm for the spent catalyst is an evidence of the attrition of the smaller sized particles thereby leading to increased coarseness of the catalyst bed. This increase in apparent particle size gave rise to a decrease in the surface area available for reaction from 251 to 118 m^2/g and could have an adverse effect on product yield as suggested by Fiske [11] and Meyer et al [19]. The Rare Earth Oxide and Sodium Oxide decreased from 1.9 and 0.3 wt% to 1.6 and 0.2 wt% respectively. These components are essential elements in creating the matrix that binds the catalyst system together. The use of Rare Earth Oxide for structural and thermal stability as well as for improving the reaction characteristics of the FCC catalyst has been reported by Vogt and Weckhuysen [22] although these could be lost through attrition because of structural deformation [23, 24].

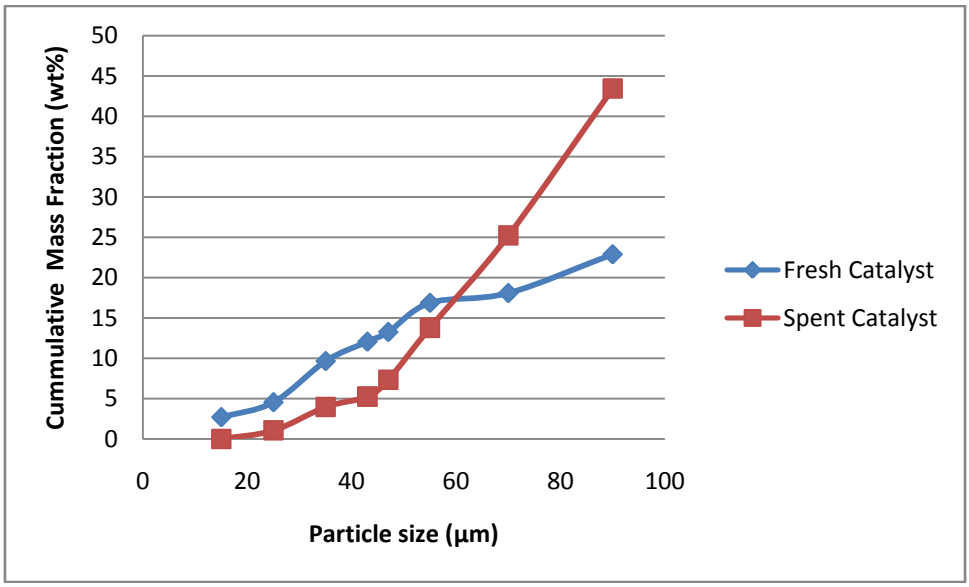
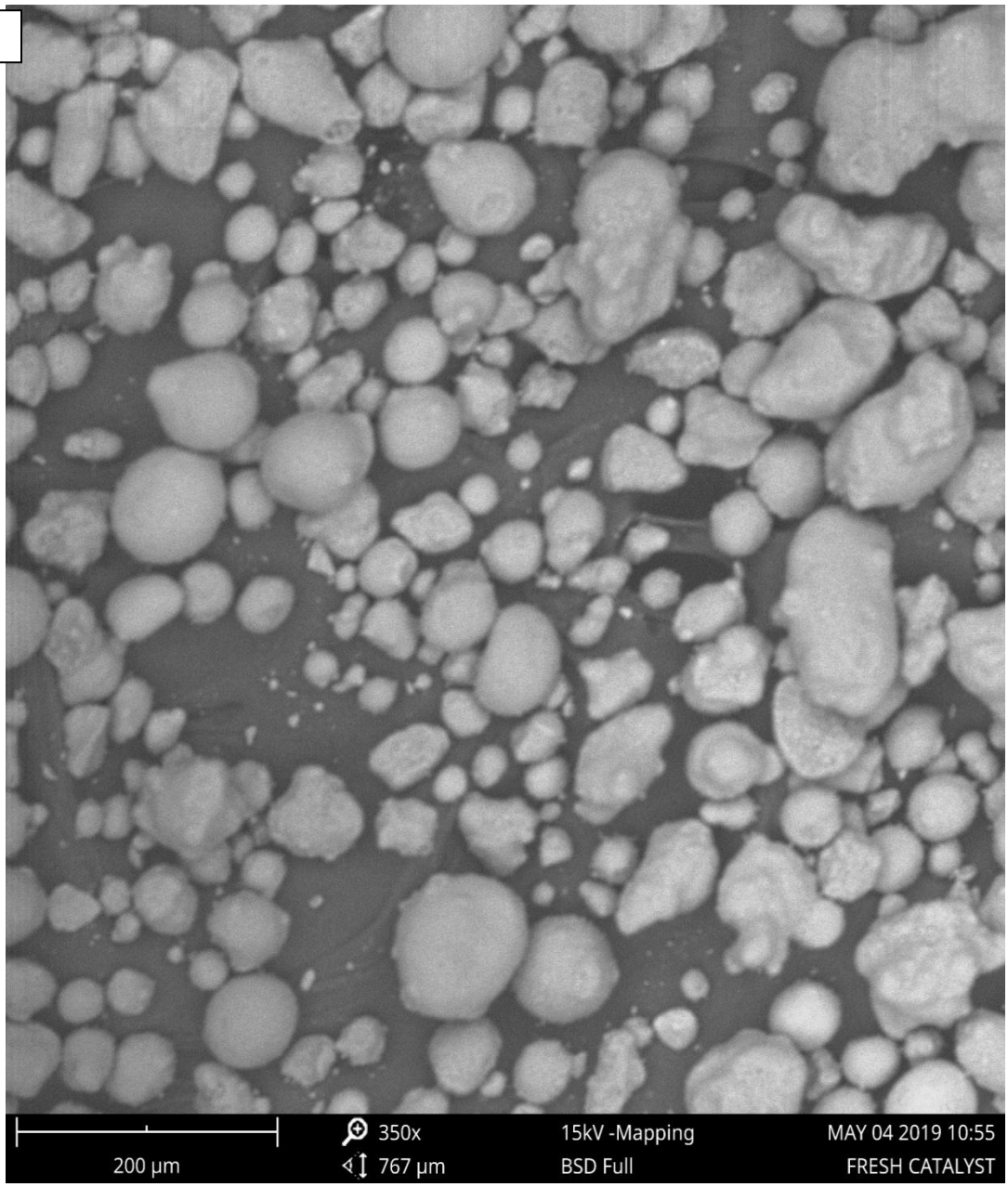


Figure 6: Effect of catalyst attrition on Particle size distribution

The particle size distribution of the catalyst before and after the FCC operation is shown in Figure 6. This figure shows a reduction in the mass fraction of the 0-60 μm sized particles of the spent catalyst as compared to the fresh catalyst. These results therefore show that the least sized particles were more attrited than the larger sized particles in accordance with the work of Thon et al [15] and therefore a further proof to the increased coarseness of the catalyst bed due to attrition. According to Coco et al [25], the resistance of this catalyst to attrition can be predicted by the ratio of the attrition indices (AI). AI (20) and AI (44) corresponding to the weight of particles generated by attrition below 20μm and 44μm. Therefore, the attrition indices for the fresh and spent catalyst from Figure 6 were found to be 58.9 and -2.50 respectively.

a.


200 µm
350x
767 µm
15kV -Mapping
BSD Full
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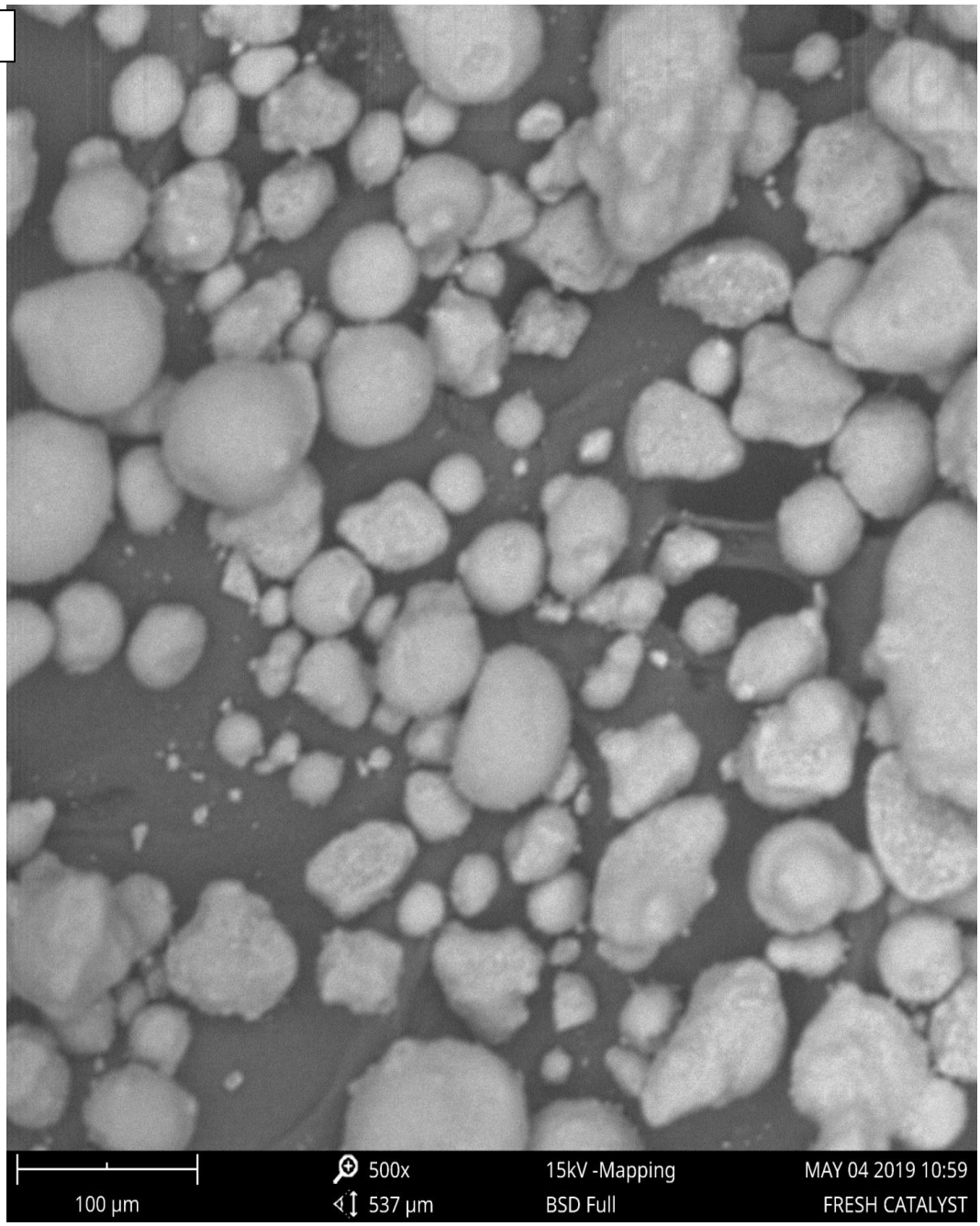
FRESH CATALYST

b.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FRESH CATALYST

c.

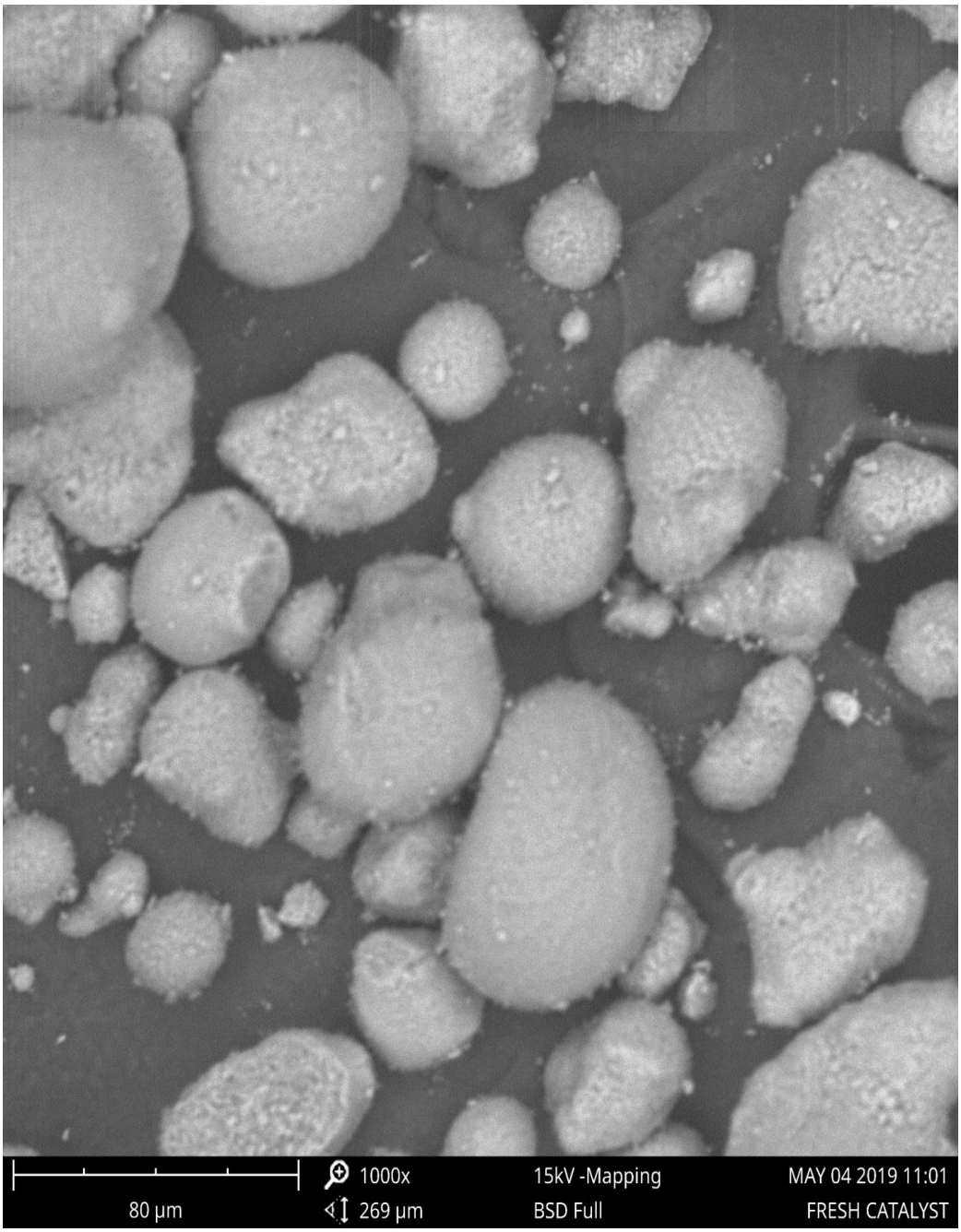
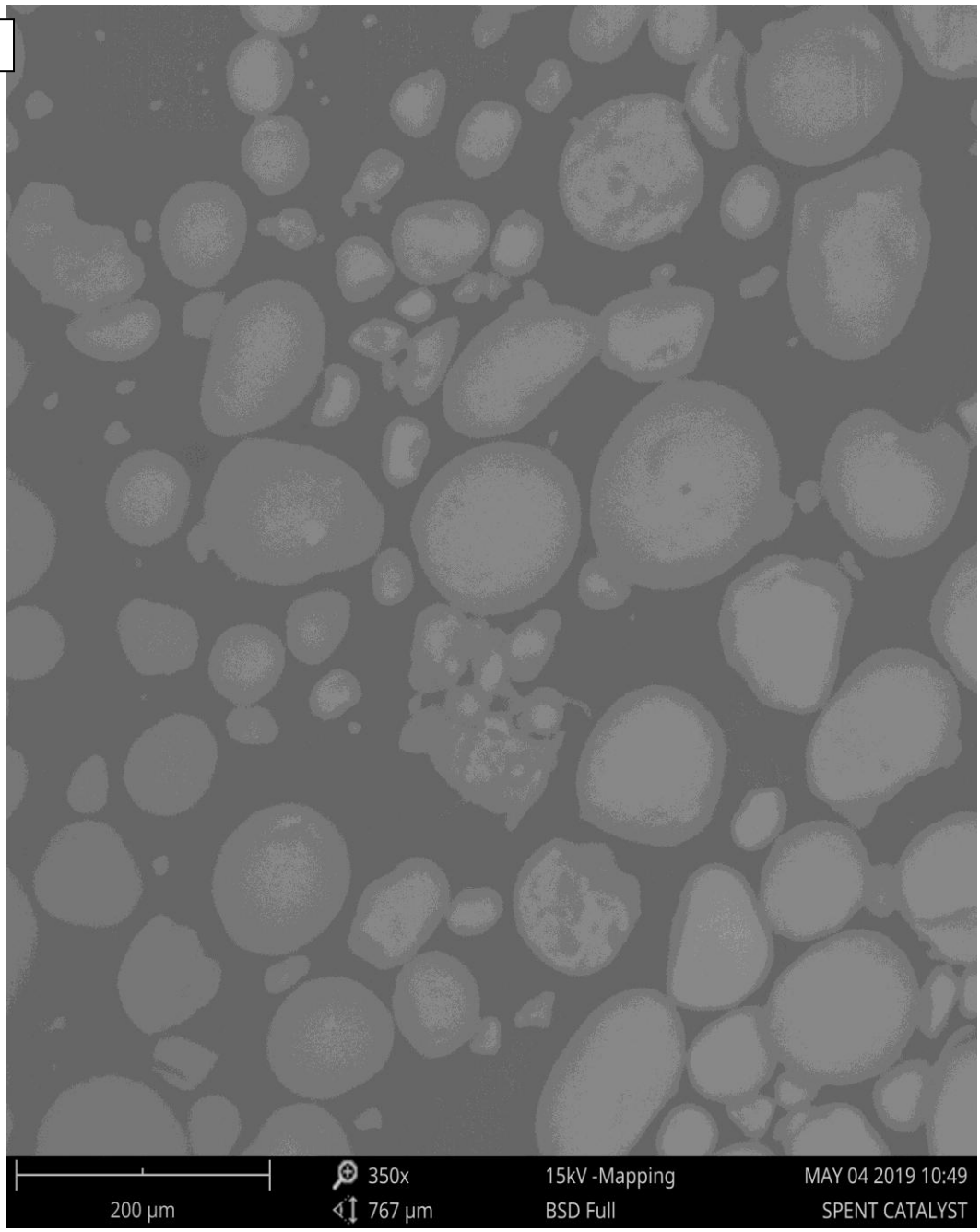


Figure 7: SEM micrographs for Fresh FCC catalyst with magnifications of (a.) 500 (b.)1000 (c.) 1500

a.


200 µm
350x
767 µm
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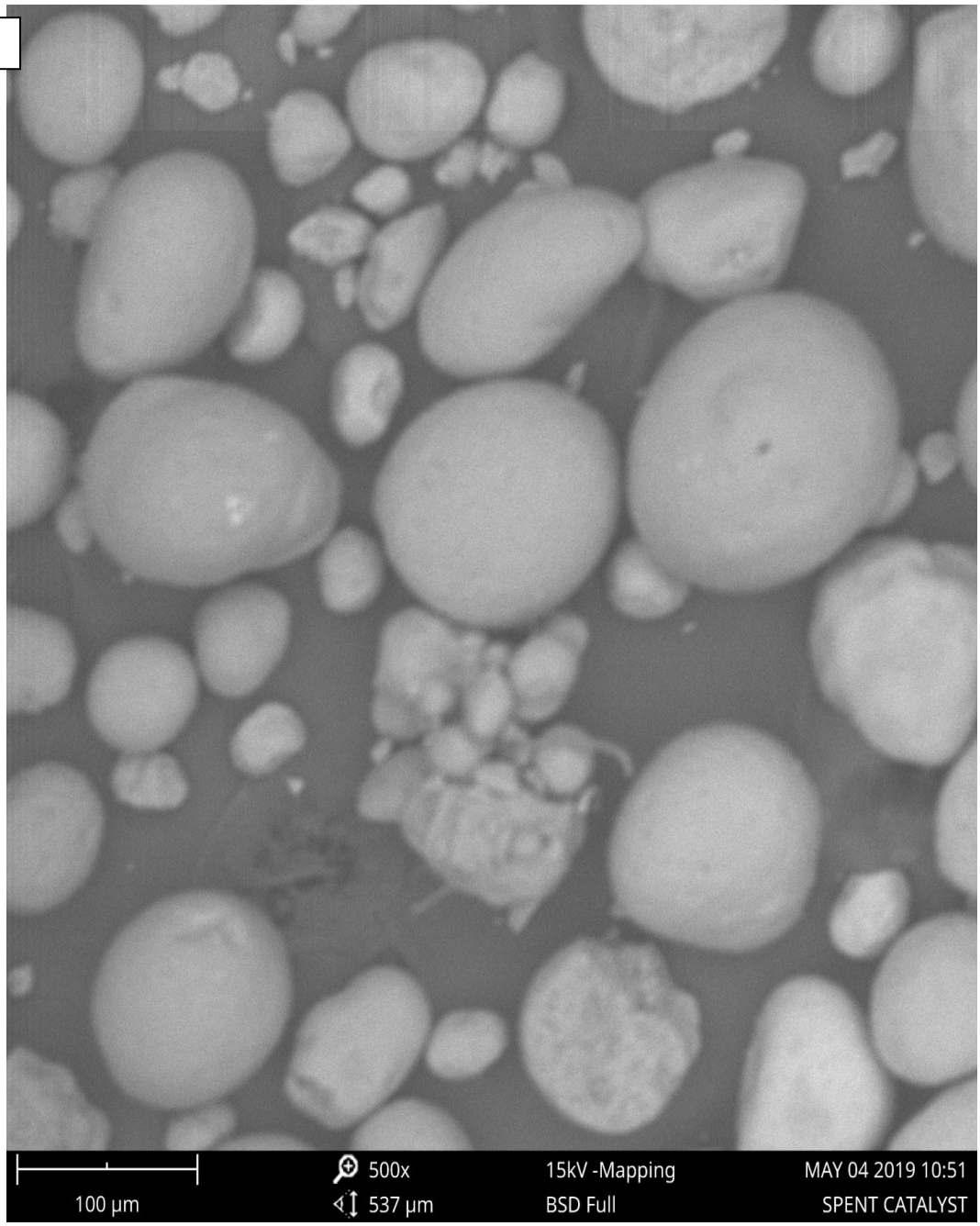
SPENT CATALYST

b.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SPENT CATALYST

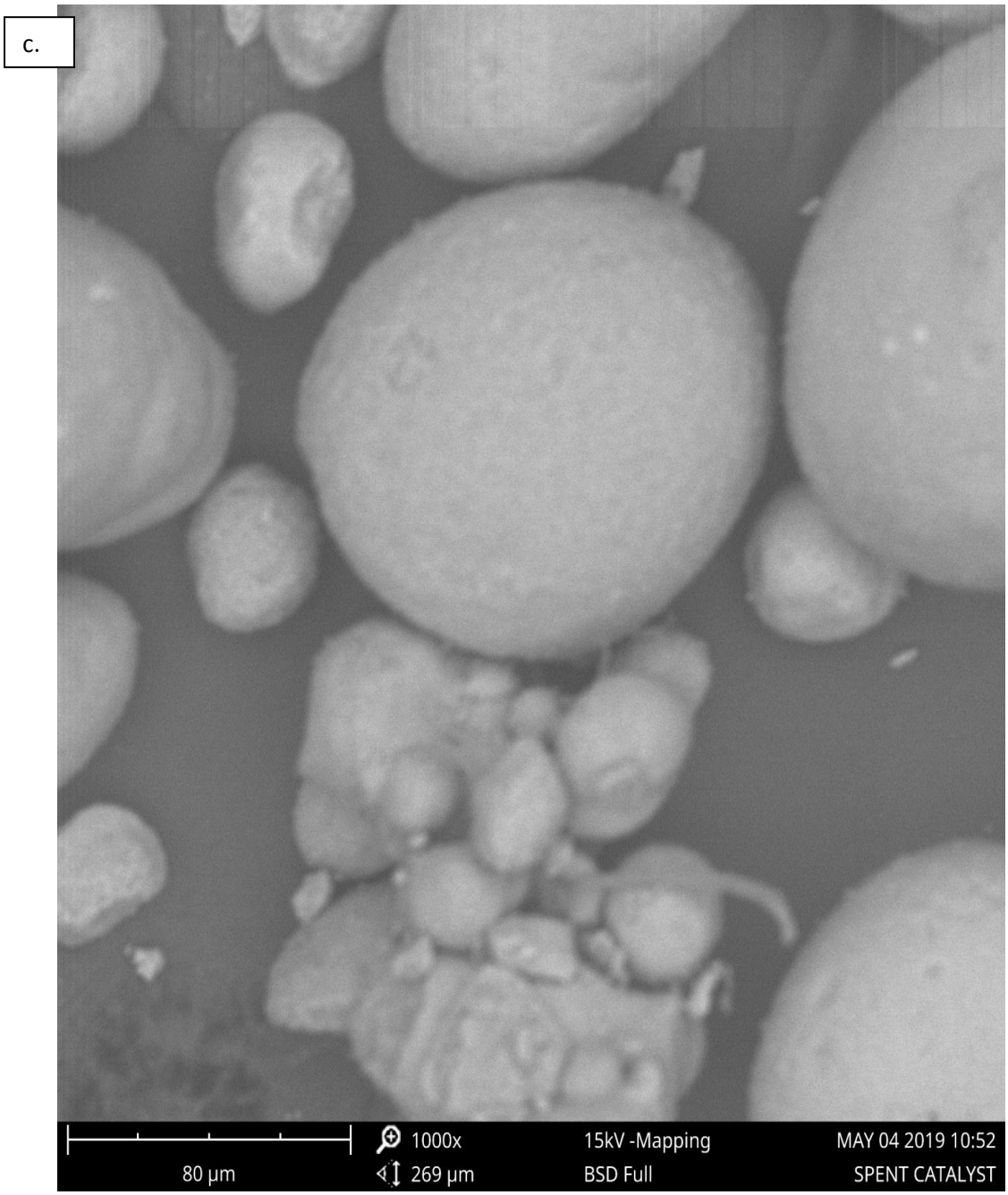

Figure 8: SEM micrographs for Spent FCC catalyst with magnifications of (a.) 500 (b.)1000 (c.) 1500

The SEM micrographs have shown the morphology of the Fresh and spent catalysts respectively (Figs. 7 and 8). Figures 7 a - c show the fresh catalyst to contain more microfine particles compared to that of the spent catalyst shown in Figures 8 a-c. For the fresh and spent catalysts, Figures 7a and 8a show the smoothness of the surface of the former over the latter which become apparently less smooth on further magnification. The work of Zhaoyong [26] established a link between catalyst attrition and catalyst poisoning by unwanted materials which could damage its smoothness and shape thereby leading to increased chances of particle collision which ultimately results in attrition.

The XRD patterns for the fresh and spent catalysts are shown in Figures 9 and 10 respectively.

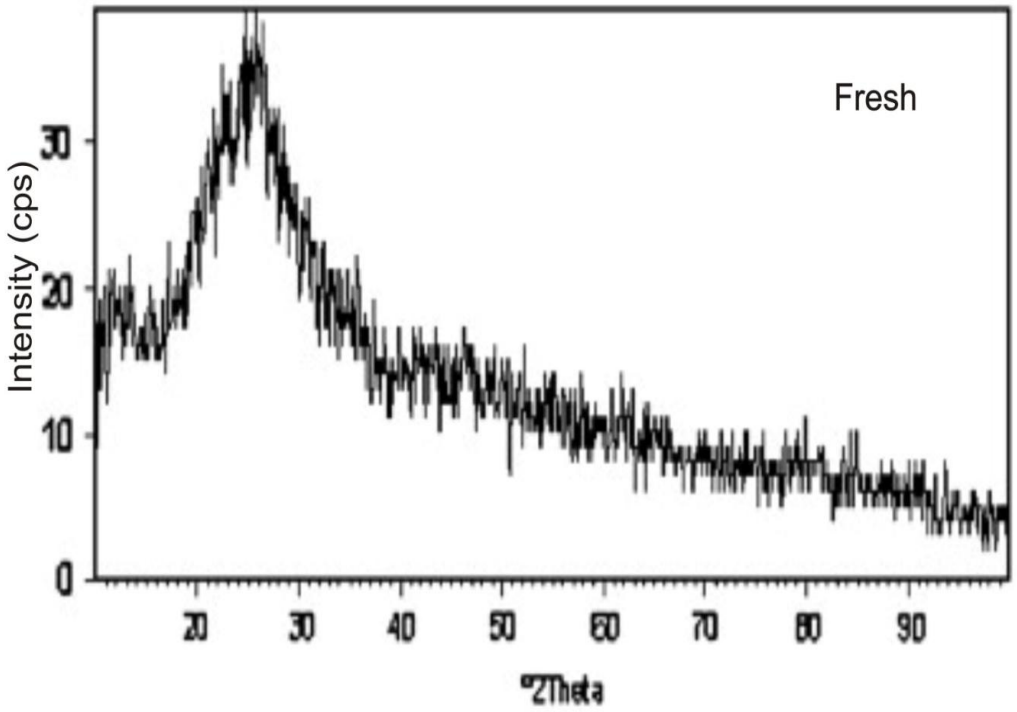

Figure 9: XRD image for Fresh FCC catalyst

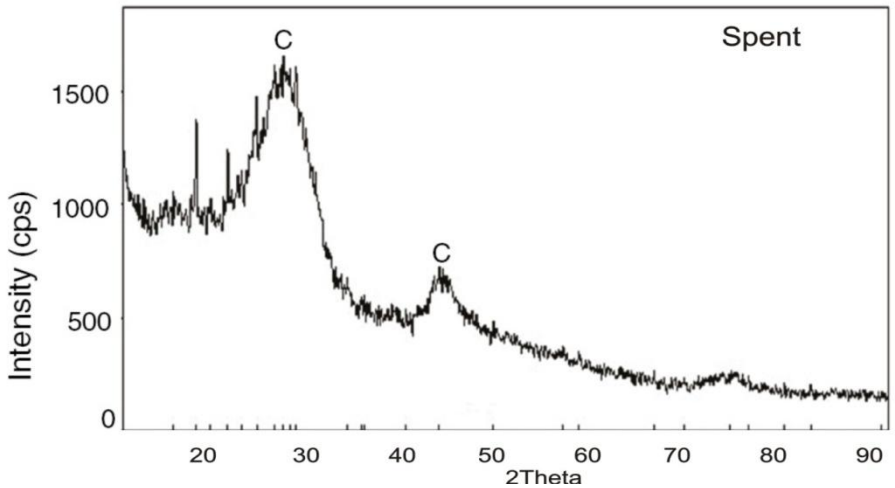

Figure 10: XRD image for Spent FCC catalyst

It can be seen that there is a significant difference in the XRD pattern of fresh and spent catalysts shown in Figures 9 and 10. Whereas the spent catalyst was dominated by the carbon peaks and other impurities retained from the cracking process which were not fully burnt off in the regeneration process, the XRD pattern of the fresh catalyst was intact and devoid of such impurities. Also, many crystalline peaks were observed for the XRD pattern of the fresh catalyst in Figure 9 whereas that of the spent catalyst (Figure 10) was dominated by the amorphous regions. The percentage crystallinity of the fresh and spent catalyst were 68.3% and 36.8% respectively. Asides the blockage caused by these carbon impurities which were retained in the catalyst pores, the loss of crystallinity of the spent catalyst could be attributed to attrition which could have distorted the catalyst structure and its crystallinity.

IV. Conclusion

From the results of this study, catalyst attrition mostly evident by catalyst losses has been observed for the industrial operation of this UOP model FCC unit. The highest pressure condition resulted in very high amount loss showing that pressure within the regenerator could have some effect on catalyst loss and the attrition process. The apparent particle size for the fresh and spent catalyst were 71μm and 75μm indicate increased coarseness of the bed whereas total surface areas of 251 μm and 118μm for the fresh and spent

catalyst respectively implies reduced surface area available for reaction in the cracking process. These were all evidences of the effect of attrition on the catalyst particles. Reduced values for the components of the catalyst such as Rare Earth Oxide and Sodium Oxide of the spent catalyst also indicate that attrition could also affect these properties. The fresh catalyst had a higher attrition index of 58.9 than that of the spent catalyst which was -2.50. Moreover, the SEM and XRD analysis also showed that the morphology and crystallinity of the catalyst particles were also affected by catalyst attrition. The least-sized particles were more attrited than the larger-sized particles.

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