Effect of Temperature on Regeneration of Deactivated Catalytic Reforming Catalyst (Pt/Al$_2$O$_3$)

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Abstract

Catalytic reforming process will continue play an important role in meeting the world's demands for high octane gasoline, petrochemicals and hydrogen hence the need to embark on continued improvement of the process. This work examined the effect of temperature on the regeneration of Pt/Al$_2$O$_3$ catalyst employed in semi regenerative fixed bed process. Samples of the catalyst were obtained from a running process (on line) at targeted periods of 10000 and 14000 hours of operation when the catalyst would have been deactivated to a degree. The catalyst samples which have undergone deactivation were regenerated at varying temperature conditions. The range of temperature studied is 400-800°C. The deactivated, regenerated and fresh catalyst samples were analyzed using FTIR, XRD and XRF to establish the extent of deactivation and regeneration. The progress of the regeneration was also monitored with gravimetric measurement of the weight losses. The work established an optimum regeneration temperature of 500°C. The optimum temperature can be employed as is a firm basis for regeneration process control and optimization.

Introduction

Catalytic reforming is a major conversion process in petroleum refining and petrochemical industries. The reforming process is a catalytic process which converts low octane naphthas into higher octane reformate products for gasoline blending and aromatic rich reformate for aromatic production. Basically, the process re-arranges or re-structures the hydrocarbon molecules in the naphtha feedstocks as well as breaking some of the molecules into smaller forms [1]. Naphtha feeds to catalytic reforming include heavy straight run naphtha. It transforms low octane naphtha into high-octane motor gasoline blending stock and aromatics rich in benzene, toluene, and xylene with hydrogen and liquefied petroleum gas as a byproduct. With the fast growing demand in aromatics and demand of high-octane numbers, catalytic reforming is likely to remain one of the most important unit processes in the petroleum and petrochemical industry. Various commercial catalytic reforming processes [2] is given in Table 1.

The basic steps in catalytic reforming involve; feed preparation, preheating, catalytic reforming, catalyst circulation and regeneration and products separation.

Catalytic reforming can be classified into the following; semi regenerative, cyclic and continuous catalytic reforming processes.

Semi-regenerative fixed bed reactors

In this type of reformers the catalyst generally has a life of one or more years between regeneration. The time between two regeneration is called a cycle. The catalyst retains its usefulness over multiple regeneration.

Cyclic fixed bed reformers

Cyclic reformers run under more severe operating conditions for improved octane number and yields. Individual reactors are taken offline by a special valving and manifold system and regenerated while the other reformer unit continues to operate.

Continuous Reformers (CCR)

In these reformers the catalyst is in moving bed and regenerated frequently. This allows operation at much lower pressure with a resulting higher product octane, C^{5+}, and hydrogen yield. These types of reformers are radial flow and are either separated as in regenerative unit or stacked one above the other.

A semi-regenerative process uses low platinum and regeneration is required only once a year. The process consists of typically three reactor beds and furnace preheaters. The dehydrogenation is highly endothermic and large temperature drop as the reaction proceeds. Multiple reactors with intermediate reheat is required. Dehydrogenation of naphthene takes place in first reactor and requires less catalyst. Preheat of feed is required. Last reactor for isomerization of paraffins [3]. Typical catalyst distribution in three reactors are 20, 30 and 50%.

Performance of the catalyst decreases with respect to time due to deactivation. Deactivation of the catalysts occur as a result of; coke formation, contamination on active sites, agglomeration and catalyst poisoning [4]. The activity can be restored through regeneration if the deactivation is because of coke formation or temporary poisons.

Process	Licensor
Rheniforming	Chevron
Power forming	ESSO Oil/EXXON
Magna forming	Atlantic Richfield Oil
Ultra forming	British Petroleum
Houdriforming	Houdry Process
CCR Platforming	UOP
Octanising	Axen

Table 1: Various Catalytic Reforming Processes.

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Catalyst regeneration is targeted at restoring high surface area and high dispersal of metal (Pt) in the catalyst. The most prevalent reactions in catalytic reforming are dehydrogenation of naphtenes to aromatics, isomerization of paraffins and dehydocyclisation of paraffins to aromatics and hydrocracking. The factors that affect these reactions are as follows [5]:

Dehydrogenation and Dehydrocyclization reaction is highly endothermic, cause decrease in temperatures, highest reaction rates, aromatics formed have high B.P so end point of gasoline. Dehydrogenation reactions are very fast, about one order of magnitude faster than the other reactions. The reaction is promoted by the metallic function of catalyst.

Dehydrocyclisation

It involves a dehydrogenation with a release of one hydrogen mole followed by a molecular rearrangement to form a naphthene and the subsequent dehydrogenation of the naphthene. The favourable conditions are: High temperature, Low pressure, Low space velocity, and Low H$_2$/HC ratio. Isomerisation: Branched isomers increase octane rating, Small heat effect, Fairly rapid reactions. This is favoured by high temperature, low pressure, low space velocity. The H$_2$/HC ratio is insignificant.

Naphthenes dehydro-Isomerisation: This is a ring re-arrangement reaction, Formed alkyl-cyclohexane dehydrogenate to aromatics. Octane increase is significant, Reaction is slightly exothermic.

Coking

Coking is very complex group of chemical reactions linked to heavy unsaturated products such as poly-*nuclear* aromatics. Traces of heavy olefines and di-olefines, high feed FBP (feed boiling point) and poor feed distribution in the reactor promote coking favored by high temperature.

Hydrocracking: This entail exothermic reactions, slow reactions, consumption of hydrogen, production of light gases and lead to coking. This is favoured by high temperature and pressure. The following variables affect the reformate yield and quality of the [2,6,7] reaction temperature, space velocity, reaction pressure, H$_2$/HC ratio and feedstocks characteristics.

In catalytic reforming temperature is considered as a critical factor; by simply raising or lowering reactor inlet temperature, operators can raise or lower the octane number of the product [8]. Moreso since all the reactor inlet temperatures are not necessarily identical, it is commonly accepted to consider the Weighted Average Inlet Temperature (WAIT). While regeneration conditions are largely controlled in CCR reforming, regeneration procedures for fixed-bed reforming units can vary widely. While all regeneration procedures share common elements, it is very common for the procedures to have evolved over years as unit configurations and throughputs have changed. Sub-optimal regeneration procedures can have a number of negative impacts on subsequent operation. Engaging a regeneration improvement study will enhance the reliability of the process and can lead to improvement in the process performance.

One of the most important factors in maintaining the overall reliability of reforming catalyst for both CCR and fixed-bed applications is to practice sound regeneration techniques. Catalyst damage can easily occur during catalyst regeneration due to the high temperatures that can occur during the carbon burning phase of the regeneration, and catalyst life can by dramatically shortened if the damage becomes excessive [9]. Other steps during the regeneration process, such as oxy-

chlorination and reduction, also play a vital role in determining the overall performance of the catalyst in the reforming unit. Optimizing each regeneration step can help to ensure the reforming catalyst will reliably perform for many regeneration cycles [10]. The refinery under study employs monometallic (Pt) on alumina base. The metal promotes dehydrogenation, hydrogenation, dehydrocylisation and isomerization reactions. The alumina base provides the acid function and it promotes isomerisation, initial step in hydrocracking and paraffin dehydrocylisation.

The present study will contribute to addressing many of the issues above considering that the refinery has aging facilities and is operating in a depressed economy.

Materials and Methods

Experimental procedures

The procedures followed were adopted from literature [11]. The catalyst chosen for this experiment were industrial fresh and two Spent A and B Pt/Al$_2$O$_3$ naphtha reforming catalyst from CRU (Catalytic Reforming Unit) of Kaduna Refining and Petrochemical Company Ltd Nigeria. The Spent A and B were collected online after 1400 hours and 1000 hours cycle of reforming operation process.

Small (1.0 g each) samples of the fresh and online collected spent A and B (were crushed using laboratory mortar and pestle to powdered form and analysis (XRD, XRF, SEM, FTIR) were done on them and recorded.

The various portions of the two Spent A and B catalysts to be used were initially weighed and recorded. Each of the various parametric study operations were boosted with nitrogen to clear any form of hydrocarbon left on the spent catalyst and other impurities, making it inert. And the nitrogen flow kept constant at 2 kg/cm^2. The two spent catalyst sourced were calcined at different temperatures (400°C, 500°C, 600°C, 700°C, 800°C), at constant air flow rate of 15 psi for a reaction time of 4 hrs each to obtain the optimum temperature.

This is to study the effect of temperature on the nature or pattern of regeneration i.e., amount of coke burnt off [12].

The elemental composition (in oxide form) of catalyst samples obtained were determined using the Energy Dispersive X-Ray Florescence (ED-XRF) machine (Minipal 4), and the X-ray diffraction (XRD) patterns were obtained using Empyreal, PANalytical diffractometer employing Cu Kα radiation (λ=0.154 nm) at the National Geoscience Research Laboratories (NGRL) Kaduna. Scanning Electron Microscopy (SEM) imaging and Surface area using sear's method were conducted at the Department of Chemical Engineering, ABU Zaria.

Discussion

The deactivated (spent) catalysts were calcined at varying temperature, time and air pressure (oxygen level) using unifactorial method to know the range of operating conditions to be used for proper regeneration of the spent catalyst. The various results were characterized using FTIR and the spectra for each operating conditions can be seen cascaded in Figures 1-4.

Comparing surface spectra of the fresh catalyst and deactivated spent catalysts subjected to different calcination temperatures. Figures 2 and 3 present the spectra of calcined Spent A and B at 400°C, 500°C and 600°C. It can be seen that the coke precursor from the deactivated spent catalyst that initially shows presence of coked catalyst (2937.68
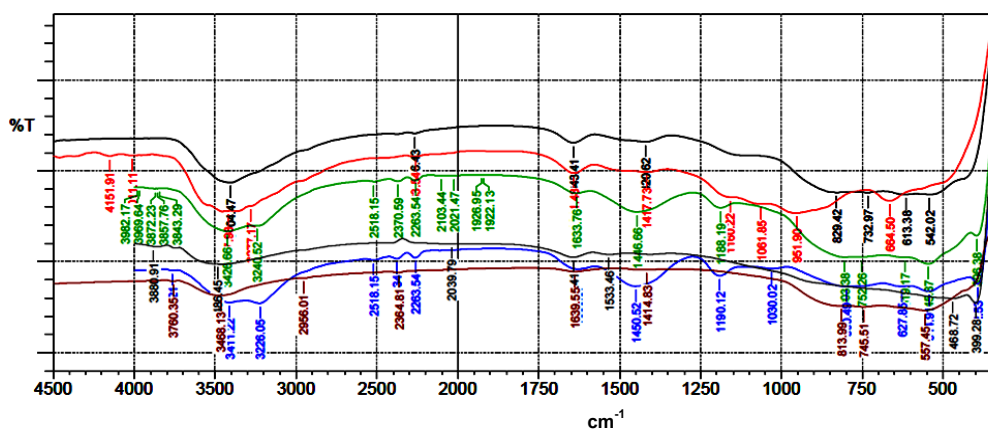
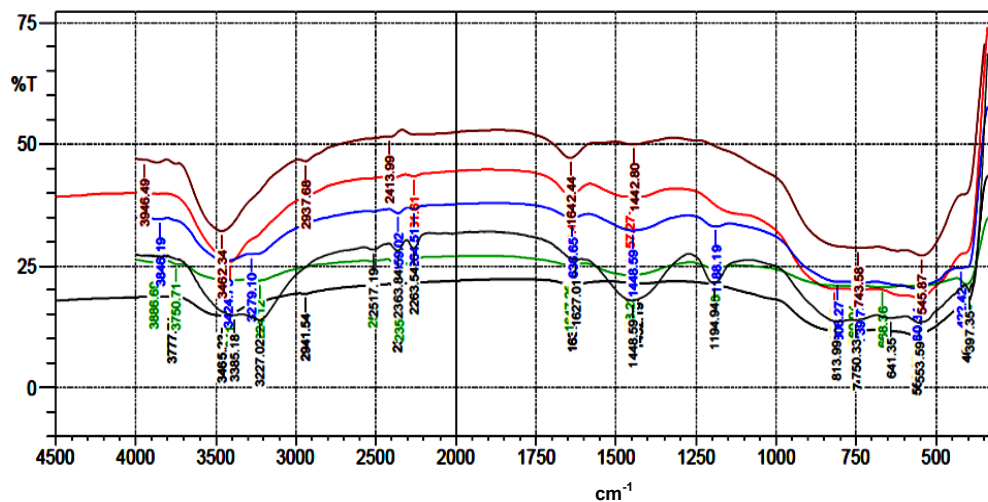**Figure 1:** FTIR spectroscopy of Fresh and Spent A at 400°C, 500°C, 600 °C, 700 °C and 800°C calcination.

Figure 2: FTIR spectroscopy of Fresh and Spent B at 400 °C, 500°C, 600°C, 700°C and 800°C calcinations.
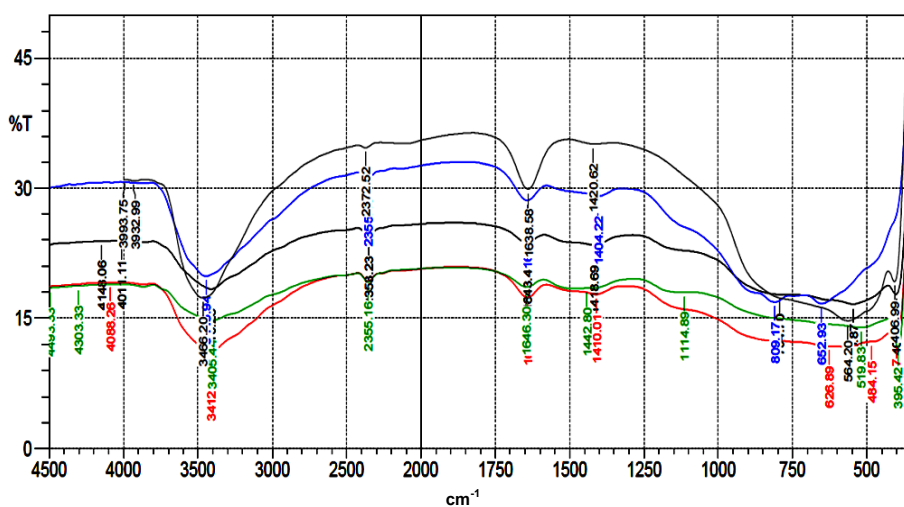

Figure 3: FTIR spectroscopy of Fresh, Spent A at 500°C for 2, 4, 6 and 8 hours calcinations.
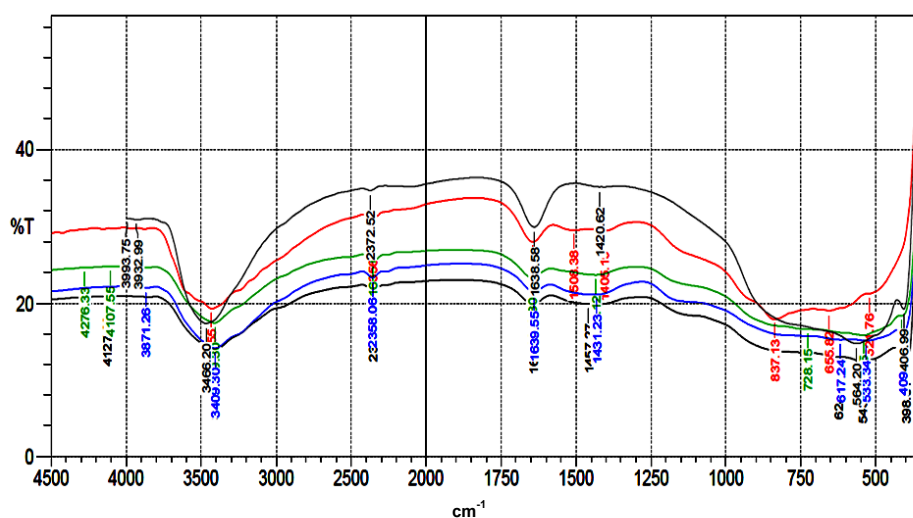
Figure 4: FTIR spectroscopy of Fresh, Spent B at 500°C for 2, 4, 6 and 8 hours calcinations.

cm^{-1} and 2946.23 cm^{-1}) in Figures 2 and 3 but after the catalyst was calcined at different temperature (400°C, 500°C and 600°C) under nitrogen gas. It shows that these coke precursors can be eliminated and there was reduction in adsorption of the olefin and the aromatic on the catalyst metal surface but much more lesser at 400°C but at calcination temperature of 700°C and 800°C in Figure 2 shows same adsorption of olefin and aromatic and much more presence of coke on Figure 5 (2956.01 cm^{-1} on Spent A) and sintering were still observed.

From these observations, it can be concluded that a lower ramp rate is much more preferred for regeneration studies and it is in agreement with most industrial application as noted by Ren et al. [13] that stated that the low temperature are usually employed to improve control the coke combustion. The temperature effect on the spent catalyst under nitrogen gas in Figure 2 of 400°C, 500°C, 600°C also produces absorption bands range 2100-2270 cm^{-1} showing small but exposed presence of CC triple bond distribution (corresponding to CC triple bond stretching) presence of combustion which is as a result of hydrocracking not needed in reforming process leading to coke formation.

Considering time variation with optimum temperature (500°C) and a lower air pressure (15 psi) chosen as a result of conditions with highest %age weight loss of deposit on the two deactivated spent catalyst. Figures 3 and 4 showing cascaded time variation for spent A and B respectively shows little or no variation change in peaks i.e., showing all functional group that can be seen in the fresh catalyst but in terms of %age weight loss for 2,6 and 8 hrs are lower compare to that of 4 hours. Meaning that coke combustion occurs more within 4 hours and reduces with any further increase in time.

The main absorption bands in Figure 6 at 3417.01 cm^{-1} (spent A) and 3410.26 cm^{-1} (spent B) corresponded OH stretching vibrations (due to OH-Pt bond) i.e., hydrogen bonded in alcohols and phenols. The absorption bands at 2359.02, 2354.20 and 2261.61 cm^{-1} has no significant effective functional group because they have weak intensity while absorption band at 1644.37 and 1641.48 cm^{-1} corresponded C=C stretching of C=C in alkenes and are possible due to the adsorption of olefin and aromatics on the catalyst metal surface [13]. This may indicate that the coke species found near the active metal are soft coke and it is mainly made up of unsaturated hydrocarbon and heavy aromatics.

Likewise, the bands observed at 806.27, 545.77, 525.62 and 399.28 cm^{-1} corresponded to chain deformation modes of alkyl group. This is in consonance with what was reported by previous workers [14,15]. The results also confirmed that, the industrial or commercial coke catalyst 3000 and 2800 cm^{-1} are missing. This shows that eliminated of these coke precursors after treatment under nitrogen gas in the presence of controlled air is possible but it can't show how active the regenerated spent catalysts except a catalyst performance test is done [16].

XRD pattern analysis

The XRD diffractograms obtained from Empyreal PANalytical Diffractometer for the catalysts (fresh, Spent A and B) are as shown in Figure 7.

The low intensity counts and the broad peaks that characterized the diffractographs of the support (γ-Al₂O₃) averred to the fact that the gamma-alumina is amorphous. The platinum catalysts have closely related bragg angles (2θs) with those of the support (alumina), but little or no significant difference with their intensity counts. The XRD diffraction peaks and bragg angles for platinum exist at 40,47,68 (Figure 7) for all the catalyst which appears to coincide with the support (gamma-alumina) which exist at 37,39,46,60,67 except that platinum shows a distinct peak at 47 and 68. These interpretations agree with the works of Hosseini [16]. The works of Yasuharu [17] also corroborated the fact of XRD pattern of platinum bragg angles of 17,40,46,67. Platinum and the Alumina are dominant as also reflected from XRF. Despite the heat effect on regeneration of the catalysts it shows that thermally the structure is not destroyed and carbon has no much significance on the structure of the catalysts.

XRF analysis

The alumina (Al₂O₃) and the platinum were more dominant and it could be seen that there was a proportional increase in the support (alumina) after reforming has taken place on the deactivated catalyst compared to fresh catalyst (89.9% to 92.23% Spent A 89.9% to 92.2% Spent B). While little decrease in platinum (2.47% to 2.38% Spent A and 2.47% to 2.13 Spent B) and loss of chlorine which was completely used up during reforming process. Majorly the fluctuation of the oxide was as a result of the loss of chlorine which was completely used up
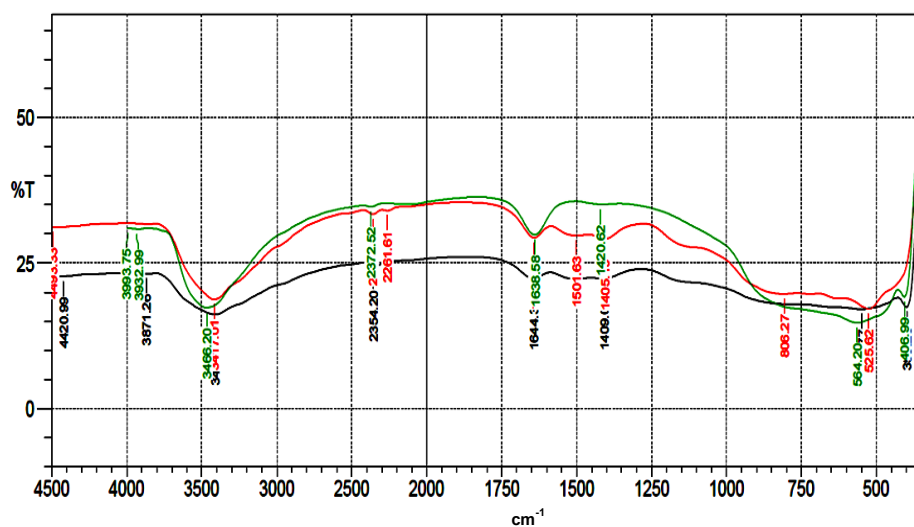
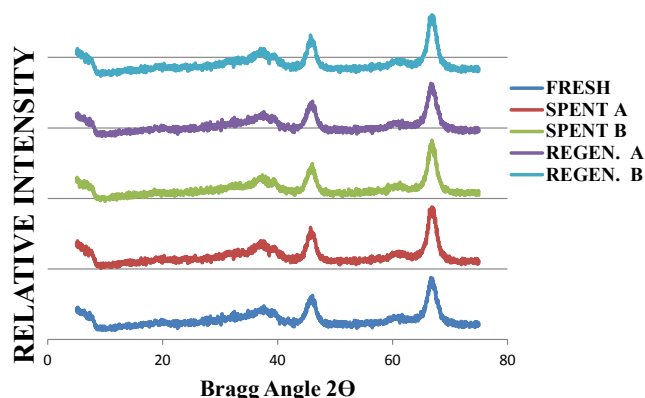**Figure 5:** FTIR spectroscopy analysis of Fresh, Regenerated Spent A and Regenerated Spent B catalyst.

Figure 6: XRD patterns of the fresh, two spent catalysts and the regenerated catalysts.

Figure 7: Catalyst Weight loss in decoking presented in weight percentage at 15 psi, 4 hrs and at various temperature range.

spreading across some of the other oxides for example alumina material increased probably as a result of chlorine loss and decrease of masses of other oxides. And due to the effect of calcinations (regeneration) burning or removal of some carbonaceous material, chlorine which was earlier used up resurfaced on the catalyst after the activity was boosted with dichloropropane and the alumina (support) decreases while other oxides too regained almost their original compositions.

The modified method used in determining the optimum conditions for regeneration were initially based on weight loss by coke burning in air at various temperatures, air flow rate and time.

Also the spent catalyst weight loss (%) were recorded and tabulated and plotted as shown in Figures 8 and 9 and Table 2 to observe the weight loss after varying each operating parameters and the best calcinations as the temperature increases from 400°C to 800°C and that of air pressure and time variation.

From Figure 8 and Table 2, the flow of air pressure was maintained at 15 psi with constant nitrogen flow at 2 kg/cm^2 for the temperature range of 400°C to 800°C for the two spe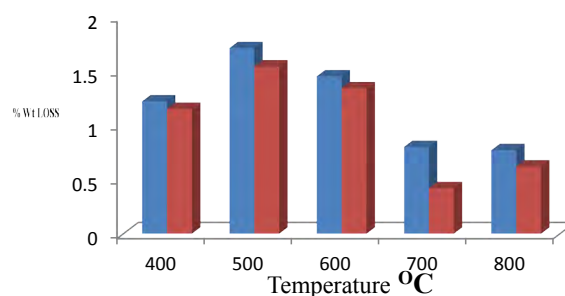nt catalyst. The weight loss during this period is due to decoking process and two set of loss was observed. The rate of weight loss between temperature 400°C and 600°C is higher than weight loss at higher temperatures (700°C and 800°C). These may be due to the nature of coke. As the temperature increases from 400°C to 600°C there were rapid weight loss far above 1% observed, showing presence of soft coke because hard coke has approximately 3.0-3.3% weight loss on catalyst while at higher temperature (700°C and 800°C) they were found to be below 1% as all shown Figure 8. But the weight loss was more at 500°C (1.72% for spent A and 1.54% for spent B) so was used as the optimum temperature for the variation of air pressure flow at 4 hours calcinations period. Figure 8 and Table 2 show that more coke was burnt off at moderately low air pressure because 10 and 15 psi gave also a soft coke presence with most %age weight loss for both spent A and B while higher air flow pressure had lesser weight loss. But 15 psi was chosen as the optimum operating pressure because it had more coke burnt off with 1.80% and 1.75% for spent A and spent B respectively. Figure 4 for catalyst weight loss in decoking presented in weight %age at optimum operating temperature and pressure and at various time range was found to all have soft coke presence no matter the time variation. But what was observed after 4 hours of calcination was the presence of no increase in weight loss of coke deposit but a little decrease as the calcination time increases (Table 3).
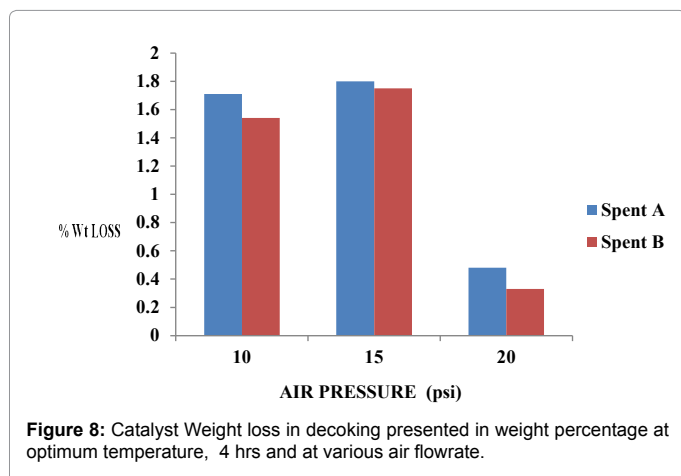
Figure 8: Catalyst Weight loss in decoking presented in weight percentage at optimum temperature, 4 hrs and at various air flowrate.
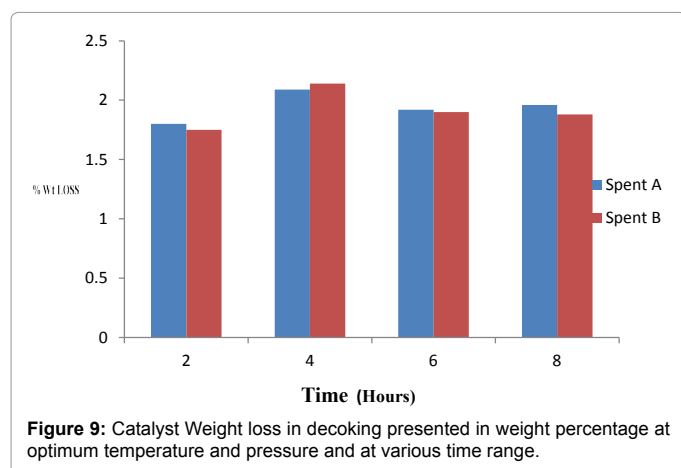

Figure 9: Catalyst Weight loss in decoking presented in weight percentage at optimum temperature and pressure and at various time range.

	FRESH	SPENT A	SPENT B	REGENERATED SPENT A	REGENERATED SPENT B
SiO_2	1.03	_	0.59	0.32	0.78
Al_2O_3	89.9	92.23	92.2	91.89	91.08
K_2O	0.01	_	0.03	_	_
Na_2O	<0.01	<0.01	<0.01	<0.01	<0.01
MgO	0.02	_	0.04	_	0.04
P_2O_5	0.78	0.64	0.48	0.68	0.59
Cl	2.95	_	_	0.98	1.08
CaO	0.278	0.322	0.269	0.301	0.265
TiO_2	0.20	0.410	0.408	0.382	0.26
V_2O_5	0.18	0.275	0.15	0.242	0.17
Cr_2O_3	0.14	_	0.13	0.09	0.13
MnO	_	_	0.025	_	0.014
Fe_2O_3	0.032	1.02	2.51	0.84	1.02
NiO	_	0.022	0.013	0.014	0.010
CuO	0.042	0.030	0.034	0.032	0.034
ZnO	0.02	0.082	0.051	0.04	0.031
ZrO_2	0.4	_	0.4	0.12	0.4
Ag_2O	0.03	0.89	0.01	0.67	0.43
BaO	0.74	0.56	0.33	0.64	0.42
ReO_7	0.1	_	_	_	_
PtO_2	2.47	2.38	2.13	2.39	2.26
IrO_2	_	0.42	_	_	_
TOTAL	99.332	99.291	99.81	96.641	99.024

Table 2: XRF of the catalysts Result of analysis (OXIDE %).

Catalyst	Weight of Catalyst (g)		Catalyst Weight loss (%)
	Before Regeneration	After Regeneration	
SPENT A	2.009	1.959	2.49
SPENT B	2.056	2.002	2.63

Table 3: Catalyst Weight loss in percentage of deactivated spent catalyst A and B after regeneration.

From Table 2, it can be seen that after regeneration of the deactivated spent catalyst A and B. that there was weight losses of 2.49% and 2.63% respectively of carbonaceous deposit on the on Pt/Al_2O_3 which shows presence of soft coke on the two spent catalyst as compared to when there is total shut down of a reforming plant for regeneration given which gives approximately 3.0-3.3% weight loss on catalyst depicting hard coke deposit.

Conclusion

The activity (i.e., effectiveness) of the catalyst in a semi regenerative catalytic reformer is reduced over time during operation by carbonaceous coke deposition and chloride loss. The activity of the catalyst can be periodically regenerated or restored by in situ high temperature oxidation of the coke followed by chlorination. Catalyst damage can easily occur during catalyst regeneration due to the high temperatures that can occur during the carbon burn phase of the regeneration, and catalyst life can by dramatically shortened if the damage becomes excessive.

In this study the effect of temperature on regeneration of Pt/Al_2O_3 reforming catalyst under use which had been deployed in operation for 10,000 and 14,000 hours were studied to establish appropriate temperature range for the regeneration which will ensure restoration of the catalyst activity. The weight loss during this period is due to decoking process and two set of loss was observed. The rate of weight loss between temperature 400°C and 600°C is higher than weight loss at higher temperatures (700°C and 800°C). These may be due to the nature of coke. As the temperature increases from 400°C to 600°C there were rapid weight loss far above 1% observed, showing presence of soft coke because hard coke has approximately 3.0-3.3% weight loss on catalyst while at higher temperature (700°C and 800°C) they were found to be below 1% as all shown Figure 8. But the weight loss was more at 500°C (1.72% for spent A and 1.54% for spent B) so was used as the optimum temperature. From the XRF analysis, the alumina (Al_2O_3) and the platinum were more dominant and it could be seen that there was a proportional increase in the support (alumina) after reforming has taken place on the deactivated catalyst compared to fresh catalyst (89.9% to 92.23% Spent A 89.9% to 92.2% Spent B). While little decrease in platinum (2.47% to 2.38% Spent A and 2.47% to 2.13 Spent B) and loss of chlorine which was completely used up during reforming process.

The XRD analysis of the regenerated catalyst showed that the XRD diffraction peaks and bragg angles for platinum exist at 40,47,68 for all the catalyst which appears to coincide with the support (gamma-alumina) which exist at 37,39,46,60,67 except that platinum shows a distinct peak at 47 and 68. These interpretations agree with the works of literature.

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These results from this work will be employed in enhancing the reliability of reforming units in refineries especially in developing countries where costs of inputs in refining operations are becoming cost prohibitive.

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