



Reactivation of Spent FCC Catalyst via Oxidation and Acid Treatment

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Abstract

Reactivation of spent FCC catalyst for its application in the adsorption of heavy metals from wastewater was investigated in this research. The most effective reactivation route of spent FCC catalyst was oxidation of spent FCC catalyst using H₂O₂ at oxidant-to-catalyst ratio of 16 ml/g, contact time of 60 minutes and a temperature of 90°C, followed by treatment with CH₃COOH solution at acid-to-catalyst ratio of 20 ml/g, 75 minutes contact time and at a temperature of 50°C. The reactivation process was monitored using the Scanning Electron Microscope Energy Dispersive X-ray (SEM-EDX), X-ray fluorescence (XRF) and X-ray diffraction (XRD). The result showed significant decreases in impurities of coke and metal, and the crystallinity of the treated spent FCC catalyst was much greater than that of the spent FCC catalyst.

Keywords: Spent FCC catalyst, reactivation, catalyst-to-oxidant ratio, wastewater, heavy metals

Introduction

There has been a consistently enormous increase in the use of FCC catalysts in the downstream sector of petroleum industries for the past 50 years [1]. Although some of these FCC catalysts, once exhausted due to deactivation can be recovered by thermal treatments, they will need to be replaced after a specific number of recoveries as their catalytic activities become extremely low. The FCC catalyst poisoned by heavy metals are usually replaced with fresh catalyst periodically because they are difficult to be regenerated [2, 3]. Oxides of rare earth metals in the FCC catalysts' structures usually provide improvement and hydrothermal stability of the FCC catalyst that enhance yields [4]. Therefore, the increase in the use of FCC catalysts over the years also translates into proportional increase in these types of oxides. While the major countries that extract and refine these oxides from their ores are China and other few countries [5, 6], the manufacturing companies of the FCC catalysts reside mainly in the USA, UK, Germany and China according to [7]. Meanwhile, the annual

production of the FCC catalysts and then the annual disposal of spent FCC catalyst (otherwise known as E-cat) are usually not made public and therefore, the exact figure is unknown. Nonetheless, annual production of about 840,000 ton has been reported from an investigation carried out lately [8, 9].

Several groups concentrated their researches on direct reuse of spent E-cat [10]. For example, it has been used as an additive for partial replacement of sand in cement or mortar powder mixtures [11]; and refractory materials, production of mineral wool and ladle covering powder in steelmaking industry [12]. It has also been used as catalysts for plastic and biomass pyrolysis/gasification or for the production of synthetic fuels but only at lab- or pilot-scale [13]. Regarding its use in cement or mortar industries, the quantity of FCC catalyst powder that can be utilized does not exceed 20 wt. % so as not to negatively affect the chemical and mechanical properties of cements and mortars. Even at that, the utilization of the spent FCC catalyst for concrete blend are still the main choices for handling of spent FCC catalysts despite the presence of highly valuable rare earths metals. Again, no updated global official data currently exists concerning the recycling rate of the spent FCC catalyst as cement and mortar additive. In summary, direct reuse of spent FCC catalyst for industrial processes is still at limited scale. Thus, the amount of spent FCC catalyst reused at present is still low compared to the huge amount disposed of annually [14].

Because of the stringent environmental criteria, this huge amount of the E-cats being disposed of annually is not acceptance. There is therefore the urgent need to find dependable methods of reactivating and regenerating the E-cat. There are very limited studies already on the use of acid treatment of the E-cats. Some of them include bioleaching of heavy metals [15]; and chemical leaching with acids like sulphuric and nitric acids [16] and citric, oxalic and gluconic acids [17, 18].

The aim of this research was to explore a proper route to reactivate the spent FCC catalyst into useful catalyst for the purpose of heavy metal adsorption from wastewater that could provide a new way for disposal and recycle of the spent FCC catalyst.

Materials and Methods

Materials

The materials used in this study were spent catalyst, Y-zeolite obtained from Kaduna Refining and Petrochemical Company (KRPC), Kaduna, Nigeria; 30 w/v % (equivalent to 8.82M) hydrogen peroxide (H₂O₂) manufactured by Guangzhou Jinhua (JHD) Chemical Reagent Co., Ltd, China; 98 w/v % glacial acetic acid (CH₃COOH) manufactured by LOBA Chimie, Mumbai, India; deionized water with about pH of 7; and 45-micron Whitman filter paper.

The equipment used was Scanning Electron Microscope Energy Dispersive X-ray (SEM-EDX, ProX by phenom-world), X-ray Fluorescence (skyray explorer XRF), X-ray Diffraction (XRD, EMPYREAN), a magnetic stirrer (78HW-1) and a drying oven.

Methods

The fresh and spent FCC catalysts were first characterized with SEM-EDX and XRF before treatment to determine the carbon and metal contents respectively.

Oxidation (Coke removal)

For the oxidation of the coke on the spent FCC catalyst surface, 8.82M H₂O₂ was contacted with the spent FCC catalyst at oxidant-to-catalyst ratios of 4, 8, 12 and 16 ml/g at a constant temperature of 25°C and a contact time of 30 minutes. At the end of each run, the sample was filtered with a 45-micron Whitman filter paper and dried in an oven at 105°C for 1 hour. Thereafter, it was characterized using the SEM-EDX to monitor the decrease in carbon content of the catalyst. The oxidant-to-catalyst ratio in the first batch of runs that gave the highest coke removal was used for second batch of runs, which were carried at contact times of 15, 30, 45 and 60 minutes, and at constant temperature of 25°C. The same procedures used earlier for the filtration and drying were used in this second batch of runs. Similarly, the oxidant-to-catalyst ratio in the first batch of runs and the contact time in the second batch of runs that gave the highest coke removal were used for third batch runs, which were carried out at temperatures of 50, 75, 90 and 100°C. Again, the same procedures used earlier for the filtration and drying were used in this third batch of runs.

Acid treatment

The acid treatment stage of the spent FCC catalyst was performed after the oxidation of the coke from the catalyst surface in order to remove any adsorbed heavy metal from the catalyst surface. First, the stock 98 w/v % CH₃COOH was diluted to reduce the concentration to 5.386M in order to increase the pH to 2 to avoid rapid dealumination of the catalyst framework. Now, the oxidized spent FCC catalyst was treated with diluted CH₃COOH at acid-to-catalyst ratios of 5, 10, 15 and 20 ml/g at constant time of 30 minutes and temperature of 25°C. At the end of each run, the sample was filtered using a 45-micron Whitman filter paper, washed with deionized water, and thereafter dried in an oven for 60 minutes at 105°C. The dried catalyst was then characterized using the XRF to quantify the residual heavy metals on the catalyst surface. The acid-to-catalyst ratio in the first batch of runs that gave the highest removal of the heavy metals was used for second batch of runs, which were carried at contact times of 30, 45, 60 and 75 minutes and at constant temperature of 25°C. The same procedures used earlier for the filtration, washing, drying and characterization were used in this second batch of runs. Similarly, the oxidant-to-catalyst ratio in the first batch of runs and the contact time in the second batch of runs that gave the highest removal of the heavy metals were used for third batch runs, which were carried out at temperatures of 50, 75, and 100°C. Again, the same procedures used earlier for the filtration, washing, drying and characterization were used in this third batch of runs.

Results and Discussion

Oxidation

The results of SEMEDX for the untreated spent FCC catalyst and the fresh FCC catalyst are presented in Figure 1. It can be seen that the spent FCC catalyst had a carbon content of 43.36 wt. % and the fresh FCC catalyst had a carbon content of 3.80 wt. %. The high amount of carbon (or coke) on the spent FCC catalyst contributed to the reduction in the catalyst activity. It should be noted that the fresh FCC catalyst is devoid of carbon. Therefore, the presence of small amount of carbon content (3.80 wt. %) in the fresh FCC catalyst might have presumably come from the SEM-EDX material.

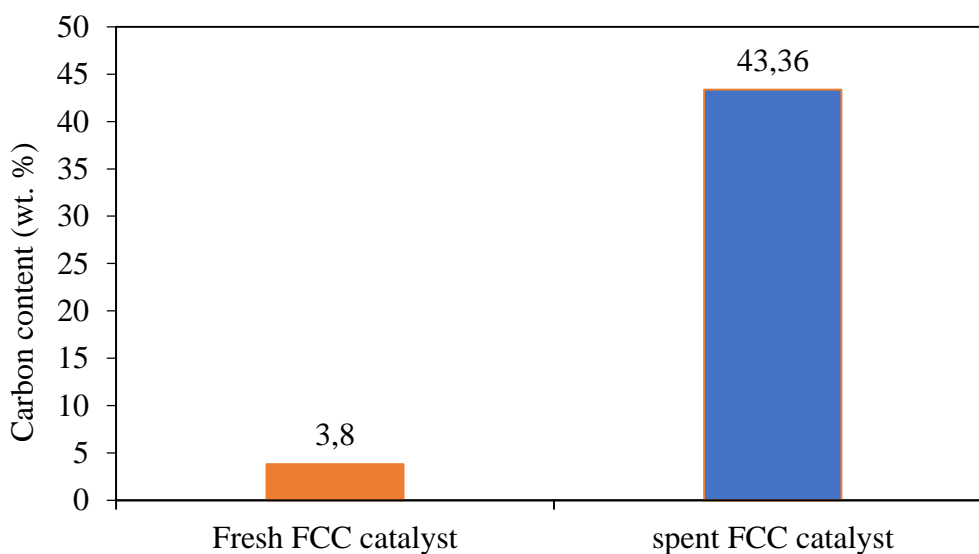


Figure 1: SEM-EDX of spent and fresh FCC catalyst

Table 2 shows the XRF results of the elemental and oxide compositions for spent and fresh FCC catalysts. These results reveal that the major components of the FCC catalyst (SiO_2 and Al_2O_3) were not significantly affected by the usage of the catalyst. Again, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the spent and fresh FCC catalysts, which were 1.64 and 1.96 respectively, were still close and according to [19], these values are within theoretical range. Meanwhile, there were significant increases in Fe and Ti contents after the use of the FCC catalyst while other metals were greatly affected. This increase can be attributed to the deposition of these metals onto the catalyst surface from the feedstock during the FCC process. The increase in the amounts of these metals on the catalyst surface leads to plugging of its active sites. Therefore, the high presence of coke and some of these heavy metals in the spent FCC catalyst calls for reactivation or regeneration.

Table 1: Elemental and oxide compositions of spent and fresh FCC catalysts

Elemental Composition			Oxide Composition		
Element (wt. %)	Fresh FCC catalyst	Spent FCC catalyst	Oxide (wt. %)	Fresh FCC catalyst	Spent FCC catalyst
Mg	0.9462	2.2621	MgO	0.9496	2.2851
Al	24.3141	27.1878	Al ₂ O ₃	32.7823	35.5433
Si	37.8161	40.0287	SiO ₂	64.1460	58.3739
Ti	0.1518	0.6807	TiO ₂	0.2532	1.1355
K	0.0071	0.1066	K ₂ O	0.0071	0.1284
Fe	0.0754	0.2928	Fe ₂ O ₅	0.1078	0.4186
Sr	0.0000	0.0065	SrO	0.0000	0.0077
Mn	0.0000	0.0076	MnO ₂	0.0000	0.0120
Nb	0.0062	0.0223	Nb ₂ O ₅	0.0089	0.0318
Mo	0.0000	0.0510	MoO ₃	0.0000	0.0765
Ta	0.0000	0.0028	Ta ₂ O ₅	0.0000	0.0035
Hf	0.0000	0.0013	HfO ₂	0.0000	0.0016
Cd	0.0000	0.0399	CdO	0.0000	0.0455
Ag	0.0022	0.0461	Ag ₂ O	0.0023	0.0495
Ca	0.0009	0.0251	CaO	0.0009	0.0352
P	0.0033	0.0307	P ₂ O ₅	0.0075	0.0703
Na	0.0072	0.0927	Na ₂ O	0.0072	0.1249
Pb	0.0000	0.0942	PbO ₂	0.0000	0.1087
LOI	36.6662	28.9983	LOI	1.7273	1.5480

Figure 2 shows the variation in the carbon removal capacity of the H_2O_2 from the spent FCC catalyst with increasing oxidant-to-catalyst ratio at a constant time of 30 minutes and temperature of $25^\circ C$. It can be seen that there was a rapid increase in the coke removal capacity of the oxidant from an oxidant-to-catalyst ratio of 4 to 8 ml/g, and thereafter a relatively slower increase in the carbon removal capacity from oxidant-to-catalyst ratio 8 to 16 ml/g. This fact may be associated with the availability of loosely adsorbed cokes on the catalyst surface that were easily removed in the initial stage of the treatment while the firmly adsorbed cokes were removed thereafter with slower rate. The highest coke removal capacity of 34.70 wt. % was observed at an oxidant-to-catalyst ratio of 16 ml/g. This is a considerable improvement compared to the carbon content of 43.36 wt. % on the spent FCC catalyst. However, the carbon content of the treated FCC catalyst was still high when compared to the carbon content of the fresh FCC catalyst of 3.80 wt. %.

Figure 3 presents the effect of contact time on the coke removal capacity of the H_2O_2 from the spent FCC catalyst surface catalyst at constant oxidant-to-catalyst ratio of 16 ml/g and $25^\circ C$ constant temperature. Removal capacity of the coke increased rapidly with time from 15 to 45 minutes and afterwards less rapidly from 45 to 60 minutes contact time. This behavior might be attributed to the fact that an increase in contact time between oxidant and catalyst gives more time for reaction between the H_2O_2 and the coke on the catalyst surface. However, the less rapid removal capacity of coke afterward might be due to the absence of loosely adsorbed coke on the catalyst surface. The highest coke removal capacity was found to be 25.96 wt. % at a contact time of 60 minutes, which is almost a 50 % reduction in the carbon content based on the initial content on the untreated spent FCC catalyst.

Figure 4 shows the effect of temperature with coke removal capacity of the H_2O_2 from spent FCC catalyst surface at constant oxidant-to-catalyst ratio of 16 ml/g and constant time of 60 minutes. It can be seen that the removal capacity increased slightly from $50^\circ C$ to $75^\circ C$ and more rapidly as the temperature increased from $70^\circ C$ to $90^\circ C$. This might be associated with the fact that with an increase in temperature, there is a reduction in film the barrier surrounding the catalyst particles enabling the oxidant to have more access to the catalyst pores thereby leading to more effective removal of the adsorbed coke from the catalyst surface. Meanwhile, the coke removal capacity remained constant from $90^\circ C$ to $100^\circ C$. This means that there would not be economic benefit in treating the spent FCC catalyst at $100^\circ C$. The highest coke removal capacity was found to be 4.53 wt. % at $90^\circ C$ and this translated to about 89.55% removal of carbon from the spent FCC catalyst.

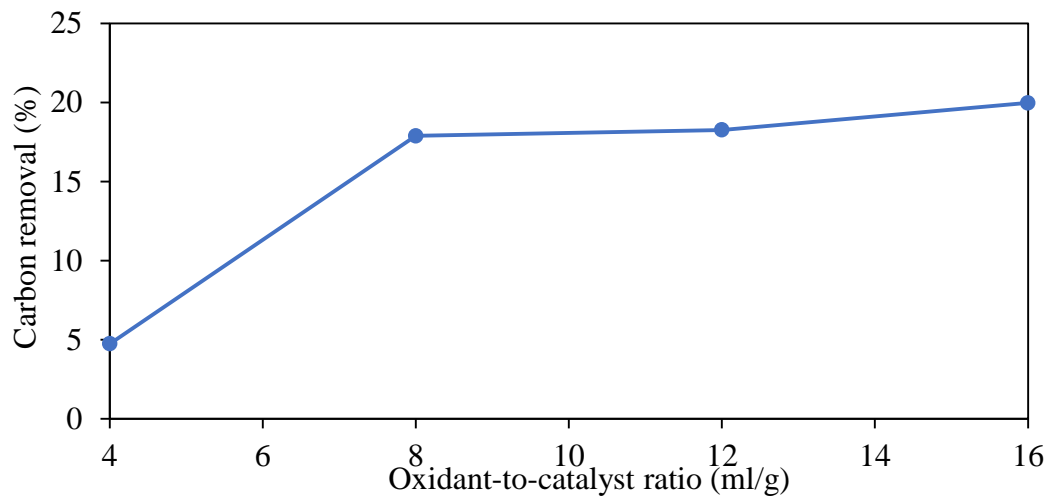


Figure 2 Variation of carbon content with increasing oxidant-to-catalyst ratio at 25°C and 30 minutes

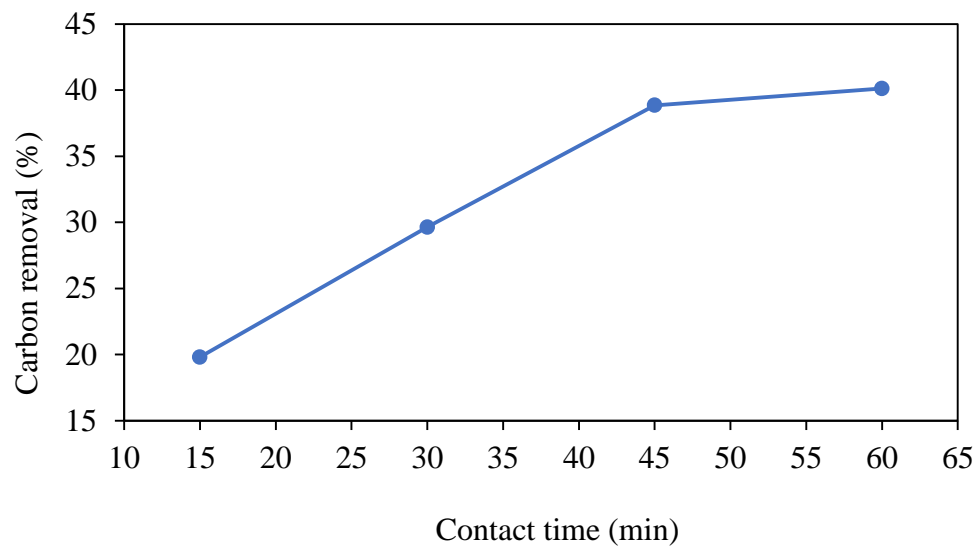


Figure 3: Variation of carbon content with increasing contact time at oxidant-to-catalyst ratio of 16 ml/g and 25°C

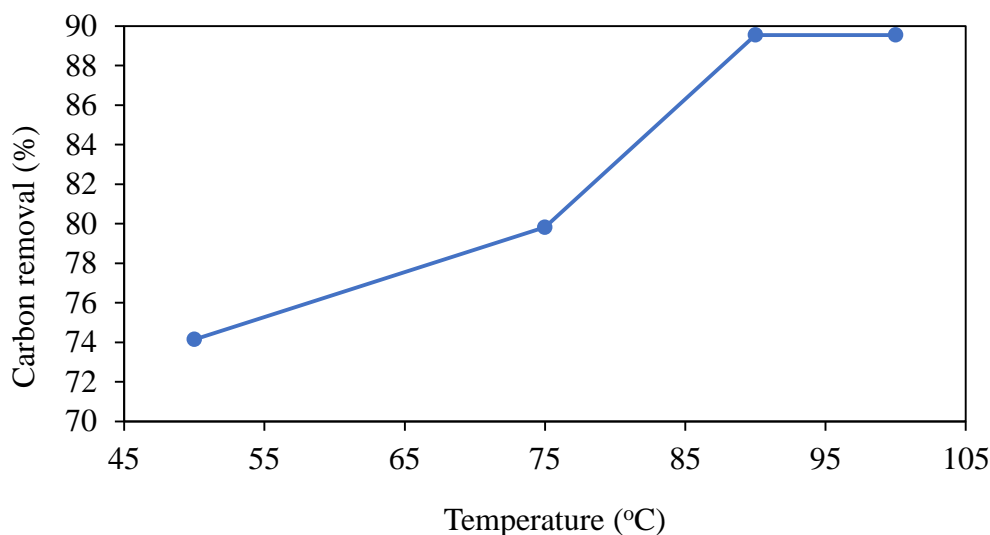


Figure 4: Variation of carbon content with increasing temperature at oxidant-to-catalyst ratio of 16 ml/g and 60 minutes

Acid treatment

As presented in Figures 5 – 7, there were general decreases in the metal contents with increase in the operating parameters during the acid treatment. However, only the reduction in Fe and Ti contents were obvious due to their high contents in the spent FCC catalyst. Figure 5 presents the result of the treatment spent FCC catalyst with CH_3COOH at varying acid-to-catalyst ratio, constant temperature of 25°C and constant time of 30 minutes. An increase in the acid-to-catalyst ratio led to a continuous decrease in the Ti content from acid-to-catalyst ratio of 5 to 20 mg/l while only a slight decrease in the Fe content was observed. This may be due to the higher content of Ti on the catalyst compared to Fe, which makes it readily available for reaction with the acid. The concentrations of the heavy metals decreased with increase in acid-to-catalyst ratio, which can be attributed to the availability of more acid volume for the formation of the metallic salts of the metals.

In Figure 6, the effect of contact time on the removal of heavy metals from the spent FCC catalyst surface at acid-to-catalyst ratio of 20 ml/g and constant temperature of 25°C is presented. The results revealed that the Ti content decreased steadily from 30 to 75 minutes contact time, while that of Fe decreased slightly from 30 to 45 minutes and then relatively rapidly from 45 to 60 minutes and again slightly between 60 to 75 minutes. This could still be as a result of relatively large quantity of Ti. The reduction in the contents of the heavy metals with increase in contact time could be attributed to the fact that increase in contact time provides sufficient time for reaction between the acid and the metals.

Figure 7 shows the effect of temperature on the content of heavy metals on the spent FCC catalyst at an acid-to-catalyst ratio of 20 ml/g and contact time of 75 minutes. Again, the heavy metals decreased continuously with increasing temperature from 50°C to 100°C . As stated earlier, increasing the treatment temperature reduces the film barrier around the catalyst hindering contact between the

acid and the catalyst, therefore increasing the treatment efficiency. It was also observed from Figure 8 that as the acid treatment progressed, there was an increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio due to the dealumination of the catalyst framework. Therefore, the optimum condition for the catalyst treatment with high heavy metal removal and less severe dealumination of the catalyst frame work was found at 20 ml/g acid-to-catalyst ratio, 75 minutes contact time and at a temperature of 50°C. This is because the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (2.30) at these conditions was above the limit of 1.5 for zeolite Y as stated by [18]. According to [20], zeolite Y with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio as given at 75°C and 100°C contain relatively less number of cation exchange sites compared to those with lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio which gives them an undesirably less hydrophilic (or high hydrophobic) surface selectivity for adsorption.

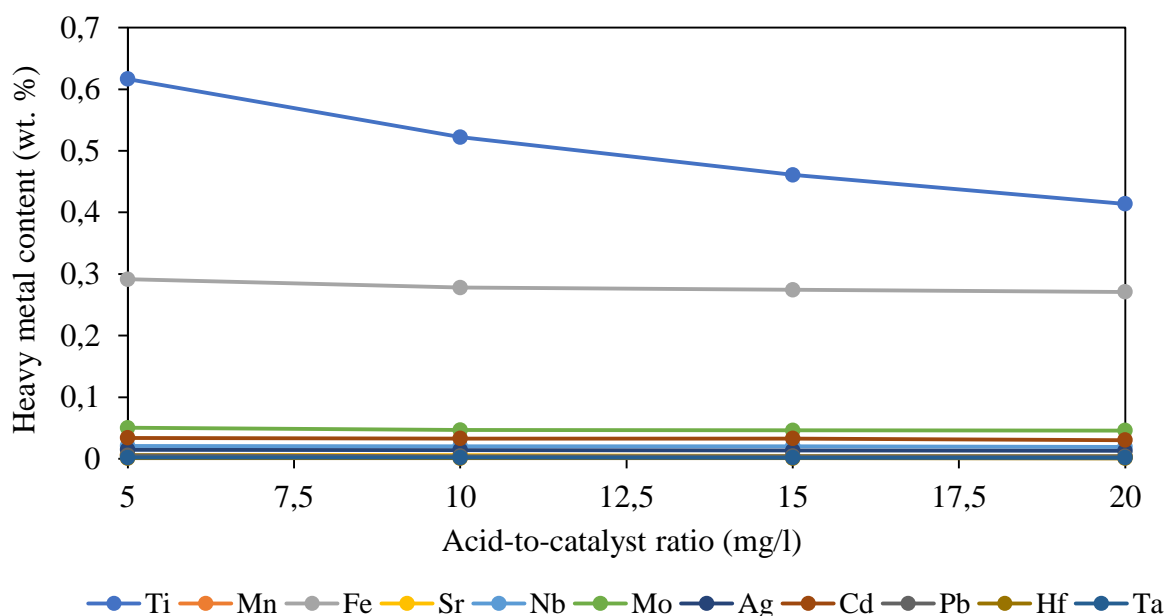


Figure 5: Variation of heavy metal contents with increasing acid-to-catalyst ratio at 25°C and 30 minutes

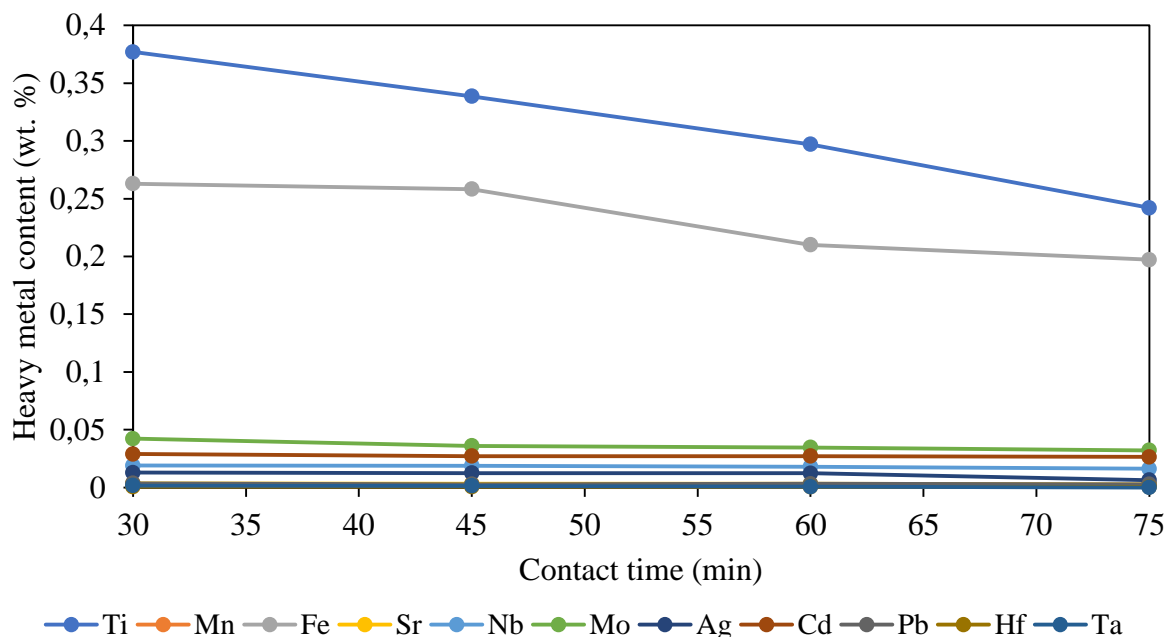


Figure 6: Variation of heavy metal contents with increasing contact time at acid-to-catalyst ratio of 20 ml/g and 25°C

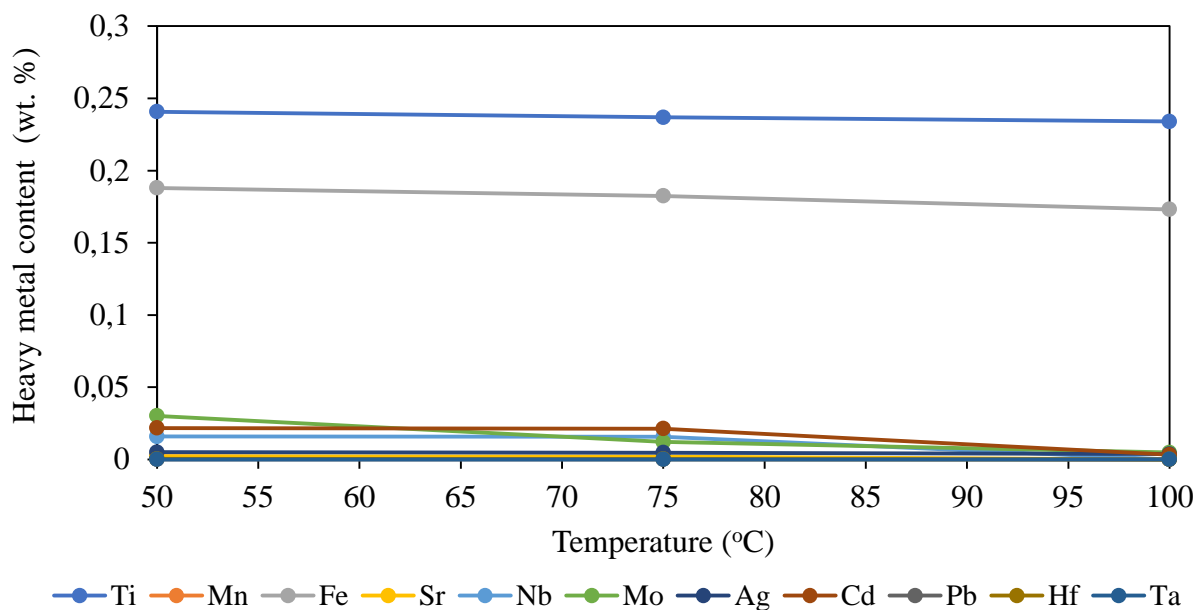


Figure 7: Variation of heavy metal contents with increase in temperature at acid-to-catalyst ratio of 20 ml/g and 75 minutes

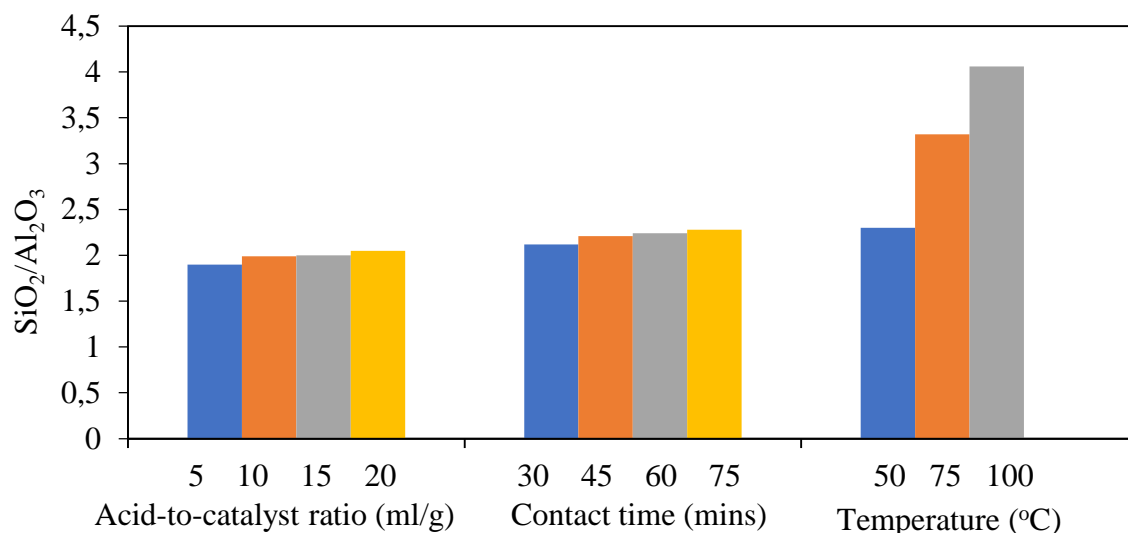


Figure 8: Variation of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of catalyst framework at different treatment conditions

The XRD patterns of the treated FCC catalyst are compared with those of spent and fresh FCC catalysts in Figure 9. This comparison shows that the method used in reactivation of spent FCC in this work has significantly improved the crystallinity of the catalyst. Quantitatively, the degrees of crystallinity of the spent and treated FCC catalysts was calculated to be 19.44% and 55.86% respectively showing also that there was a significant improvement in the catalytic properties of the treated catalyst. However, it can be seen that the crystalline peaks of the treated catalyst were still much lower than that of the fresh catalyst. This could be because of sintering of the catalyst surface due to high temperature or abrasion of the catalyst particles against each other during the FCC process.

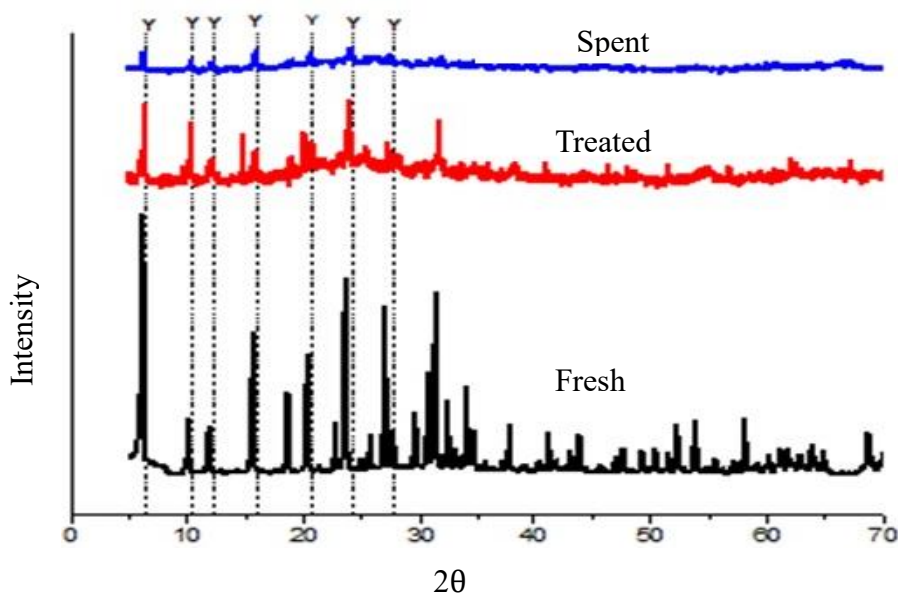


Figure 9: XRD patterns of spent, treated and fresh FCC zeolite Y catalysts

Conclusion

The reactivation of spent FCC catalyst through oxidation and acid treatment was carried out with the following conclusions drawn from the results.

- The most effective oxidation condition was found at oxidant-to-catalyst ratio of 16 ml/g, contact time of 60 minutes and temperature of 90°C. This condition produced about 89.55% of carbon removal.
- The acceptable acid treatment condition was found at acid-to-catalyst ratio of 20 ml/g, 75 minutes contact time and temperature of 50°C. This condition produced about SiO₂/Al₂O₃ ratio of 2.30, which was an indication of insignificant dealumination of the catalyst framework and hence the strong hydrophilic surface selectivity of the catalyst was still preserved.
- There was significant improvement in the crystalline peaks of treated catalyst when compared with that of spent catalyst.

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