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Catalyst Based on Sludge Derived from Wastewater Treatment of Textile Industry

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Study of the catalytic properties of residual sludge from effluent treatment plants of two textile industries -located in Quito Ecuador- with different dye finishing processes. The sludges were firstly dried at 110, 125 and 140°C to analyze the effect of the temperature on the mechanical strength, then they were calcined at 300, 600 and 900°C to verify the influence of the calcination temperature on the surface properties. The structural characterization was performed with: elemental analysis, infrared spectroscopy FTIR, nitrogen adsorption, X-ray diffraction, programmed temperature reduction TPR and SEM images. The catalytic properties were studied with a thermal decomposition of glycerol and different types of oil. It is concluded that the best conditions to obtain a catalytic material from these residual sludges, were: 110°C and 600°C for drying and calcination, respectively. The catalyst with a specific area of 31.73 m^2/g and presence of Cr^{2+} and Zn^0, provided higher weight loss in the thermal decomposition reaction for glycerol and the catalyst with the specific area of 30.36 m^2/g and a metallic content of Fe^0 promotes higher decomposition for heavy hydrocarbons. Due to the metallic content, and the physisorption and chemisorptions capability the residual sludges of textiles industries have catalytic activity and can be used for hydrocarbon decomposition.

1. Introduction

The textile industry has had an important participation in the World`s economy in the last years mainly in developing countries, where it has generated jobs and has become the second most important manufacturing sector. However, textile industry involves multiple transformation processes of raw materials, in which the consumption of hazardous chemical substances, mainly in the dyeing and finishing, is the cause of contamination in the effluents. Consequently, these effluents should be treated before being poured into channels or sewage. Textile industry generates a large number of solid wastes, mostly primary and biological sludge from wastewater treatment systems. The most common pollutants in those wastewaters are: metals, non-degradable surfactants, toxic organic substances (phenols, aromatic solvents, chloride, perchloroethylene, oxalic acid among others) and dyes (Environmental Technology Program for Industry, 2007).

It has been reported that the amount of daily discharge of textile dyeing sludge (TDS) had exceeded 20,000 t as wet sludge (with moisture of 80 %) just for China in 2013, and the situation is also severe in other countries like India, Japan, and Indonesia. Sludge is produced because of the wastewater treatment; it concentrates the pollutants originally present in the wastewater. These pollutants can react chemically with other compounds and due to their characteristics, they affect the environment. These sludges are classified as hazardous industrial waste because it contains significant amounts of heavy metals, which could cause disposal problems, such as contamination of the soil surface, phytotoxicity and the increase of potentially toxic elements in the trophic chain. On the Basel Code, the sludges resulting from effluent treatment that contains hazardous substances are classified as Y18, which means that these wastes must be controlled.

Nowadays, waste valorization studies have focused in the search for alternatives to convert the sludge into useful materials, mainly due to the few areas for its final disposal and problems with the atmospheric pollution derived from the incineration of the industrial waste. In addition, traditional methods of sludge management are increasingly complex and expensive.

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Some sludges with very different characteristics are susceptible to being reused or revalued as soil improvers (compost) or they can be used for the recovery and recycling of elements present in them. Klose et al. (2000) obtained catalytic materials derived from sludges of the tannery, textiles, and galvanizing processes and the activity of the catalysts were evaluated in reactions with propane. Also, Sushil et al. (2011) highlighted that waste derived from the aluminum industry could be synthesized to be applied in the oxidation of propane. Finally, Herrera et al. (2013) proposed the synthesis of catalytic materials for the dehydrogenation of propane from textile sludge and automotive galvanizing processes. By considering these issues, the main objective of this work is to obtain catalytic materials derived from the residual sludge of waste treatments of the textile industry and evaluate them on the thermal catalytic decomposition of two types of hydrocarbons (HC).

2. Experimental

Two types of sludges from two different textile factories located in Quito-Ecuador have been analyzed. The first one is based on cotton, polycotton and polyester dye and its water treatment is focused on electrocoagulation. The second one is based on jean-like fabric, this water treatment focused on flocculation and coagulation systems. For each industry, the sludges were identified as LR-1 and LR-2, respectively, and the catalytic materials derived from these sludges were named C1 and C2.

2.1 Catalyst synthesis

The sludge was dried at 110 °C; this temperature was previously defined as the most proper in the range of 100 - 140 ºC, due to it provides the highest mechanical resistance. Then, the dried sludges have been sieved at 150 - 250 μm. To remove non-desired elements, such as organic material, and to oxidize the metals present on the dried sludges, the samples were calcined at 300, 600 and 900 ºC, during 3 h with a temperature ramp of 8 ºC/min. The materials obtained from this thermal treatment have been considered as catalytic material. Prior to verifying the catalytic activity of these materials, they need to be reduced in an atmosphere of 10 % H_2/Ar and at the same temperature of calcination process.

2.2 Catalyst material characterization

The content of CHNS, were measured by high-temperature combustion principle (Elementar, Vario Macro Cube).The physical properties (BET surface area and pore volume) of dried sludges and catalyst materials were analyzed by N_2 adsorption-desorption (Horiba, SA-9600).

Fourier-transform infrared spectroscopy (FTIR) has been used for detecting functional groups and characterizing covalent bonding information in the catalytic materials (Perkin Elmer, Spectrum Two).

Metallic elements were identified with the X-ray diffraction (XRD) analysis (PANalytical EMPYREAN). Scanning electronic microscopy with electronic dispersive spectroscopy (SEM/EDS) was used to study the surface morphology and chemical metallic composition of the catalytic materials (TESCAN, MIRA3, X500), these experiments have been done at CENCINAT- ESPE Laboratory. Atomic absorption spectroscopy (AAS) enabled to quantify the metallic content of the catalytic materials (Perkin Elmer, AAnayst 400), the samples were digested on a microwave digestor (MILESTONE ETHOS UP).

Temperature programmed reduction (TPR) and CO pulse Chemisorption have been performed to verify the catalytic properties. For TPR, a stream of 10 % H_2/Ar has been used, the samples had to undergo a heating rate of 10 °C/min until 1000 ºC to verify the reduction peaks of the catalysts. CO pulse chemisorption capacity of C1 and C2 has been carried out with a stream of 10 % CO/He, heating ramp of 10 ºC /min, and pulses until the saturation at 400 ºC (Micromeritics Autochem 2920).

2.3 Evaluation of catalyst properties

A thermal catalytic reaction of decomposition of hydrocarbons (HC) has been achieved to analyze the catalyst properties. Glycerol (Panreac), and desalted oil (Petroecuador) have been evaluated by a Thermogravimetric Analysis (Mettler Toledo, TGA1 SF/1100). High weight lost represents high catalytic activity. Samples of both catalysts have been tested in a space-time of 0.15 $g_{catalyst}/g_{HC}$. Thermal catalytic decomposition of glycerol and oils have been carried out at 250 ºC and 600 ºC, respectively

3. Results

3.1 Determination of calcination temperature

The thermal treatment applied to the sludges should ensure that the synthesized catalyst have physisorption and chemisorption capacity. The calcination reduces the organic material and oxidizes the metal present on the sludges. Table 1 illustrates the elemental analysis for dried sludges (at 110°C) and catalytic material calcined at 300, 600 and 900 °C. The CHNS are present in the sludges and in catalytic materials and these quantities are reduced when the calcination temperature increased. The sulfur levels can cause poisoning of the metals in the catalyst. C1 has more sulfur content, probably due to it is derived from a textile industry which dyes cotton and polycotton by means of sulfide dyes processes.

Table 1: Elemental content and physisorption characteristics of dried sludges (LR1-LR2) and catalyst materials (C1-C2)

Material	Temperature [°C]	%C	%H	%N	%S	Surface area [m^2/g]	Pore volume [cm^3/g]
LR1	110 (dried)	9.89	2.84	0.83	2.65	136.51	0.181
C1	300	5.39	0.71	0.69	2.61	135.72	0.158
	600	0.31	0.01	0.04	2.39	30.36	0.038
	900	0.16	0.00	0.03	0.92	0.00	0.000
LR2	110(dried)	8.79	1.48	0.41	0.47	59.41	0.075
C2	300	6.97	0.73	0.39	0.46	45.39	0.066
	600	3.20	0.20	0.05	0.44	31.73	0.052
	900	1.11	0.00	0.03	0.34	3.48	0.007

The effect of the temperature on the surface area reduction can be observed. The catalytic activity is largely influenced by the physisorption capability, for this reason, low surface area and pore volume can reduce the use of this materials as a catalyst. Surface areas of the material synthesized have been comparable with the metal supported catalyst. Klose et al. (2000) have been obtained materials between 0.97 and 35.90 m^2/g.

At 600 °C, both C1 and C2 have similar physisorption characteristics and low organic material content, therefore, this temperature is selected for the calcination procedure. Similar calcination temperatures are defined by Amin and Yusup (2015), Herrera et al. (2013) and Klose et al. (2000) for other waste derived catalyst.

3.2 Metal content in the catalytic material

FTIR assays have been performed for the calcined material. For the C1, it has been identified the defined peaks at different wavelengths: 400 and 750 cm^{-1}, which correspond to metal-oxygen bonds, 1,128 cm^{-1} to Si-O-Si bonds (Jindarom et al., 2007), it is noted that this peak tends to be reduced while the calcination temperature increases. At 435; 560 and 1,600 cm^{-1}, it was identified the ferric oxide (Vahur et al., 2010). No changes were observed while the temperature increased. Other oxidizes as Cr_2O_3 (435 cm^{-1}) and ZnO (2,930 cm^{-1}) were identified. For C2, there are some similarities with C1 as the presence of metal-oxygen like Fe_2O_3; other peaks as calcium carbonate at 873 and 1,422 cm^{-1} were identified, this peak disappears at 900 ºC, likely due to the $CaCO_3$ decomposition at high temperatures. Other peaks in 1,590 and 2,926 cm^{-1} were observed due to the zinc oxide (Abrokwah et al., 2016). The Cr_2O_3 at 460 and 790 cm^{-1} are in this catalyst. These results permit to identify in C1 the presence of Fe mainly, and in C2, the presence of Cr.

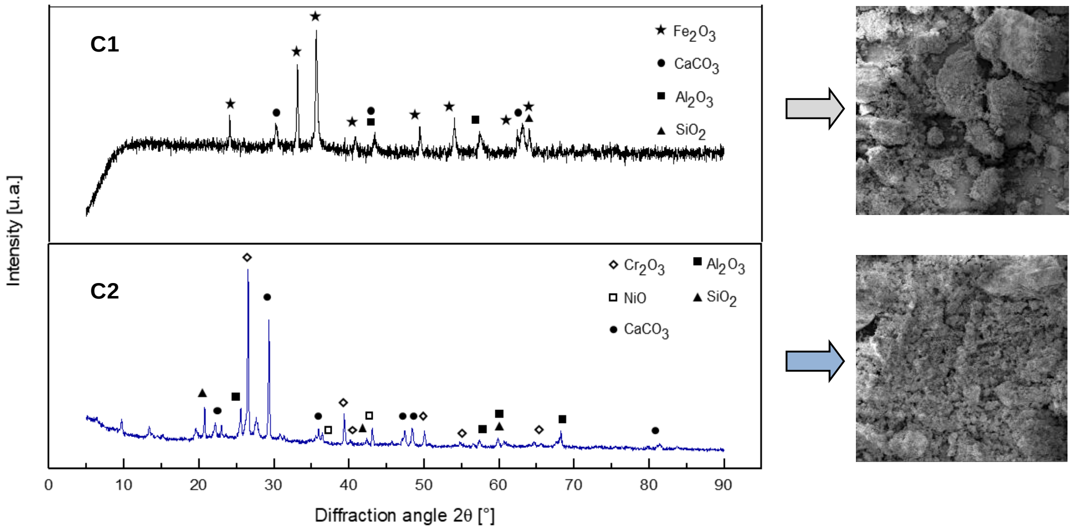

Figure 1: XRD profile and SEM images for C1 and C2 catalysts calcined at 600 ºC.

X- Ray Diffraction (XRD) confirms the presence of the metals in both catalysts, as shown in Figure 1. C1, has Fe_2O_3 defined peaks on diffraction angle: 2θ = 33 and 35°. C2 has two peaks: Cr_2O_3 on 2θ = 27° and $CaCO_3$ on 2θ = 29°. The previous results can show the dominant presence of Fe in C1 and both Cr and Ca in C2. These values were quantified by atomic absorption, the results were:0.9 %w Fe in C1 and 0.1 % of Cr and 0.5 % of Ca in C2. The presence of these metals was confirmed by SEM/EDS, in this sense, 73.3 % of Fe was identified on the surface of C1 while 55.15 % of Ca and 5.65 % of Cr were identified on the surface of C2. Similar metals were identified by other textile and automotive sludge (Herrera et al., 2013).

SEM images of both catalysts are shown in Figure 1 (right side), as it is observed C1 has well-structured particles and higher size compared with C2, likely, influenced by the water treatment process, from which the sludges are obtained. C1 was derived from an electrocoagulation treatment, which promotes the particles structuration.

3.3 Chemisorption capacity of the catalytic material

H_2-Temperature programmed of reduction and CO-pulses (Figure 2) has been done for analyzing the chemisorption capacity of the catalyst. For C1 two peaks of reduction are identifying at 535 °C which corresponds to the reduction from Fe_2O_3 a Fe_3O_4 and at 800 °C for reduction to Fe_3O_4 at Fe^0 (Costa et al., 2010). For C2 a peak at 567 °C corresponds at the reduction from Cr_2O_3 to CrO (Carriazo et al., 2010) and the other peak at 715 °C from ZnO to Zn^0 (Pérez et al., 2005).

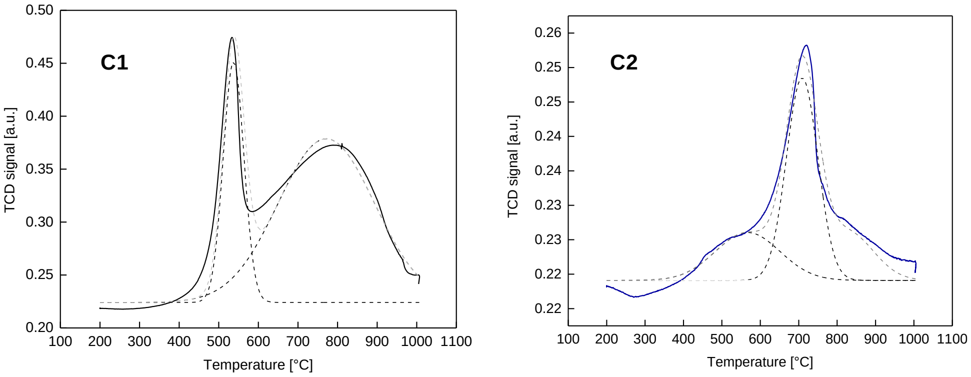

Figure 2: TPR profile for C1 and C2 catalysts calcined at 600 °C

The reduction capability of the metallic content with H_2 verifies the catalytic activity of the derived sludge catalysts with metallic active sites, these materials can be used for thermal decomposition of hydrocarbons (Kosivtsov et al., 2016) and other processes like steam reforming (David, 2015)

The CO pulses shown in Figure 3 ratify that the C2 has more adsorption than the C1. These results confirm the catalytic activity of chemisorption of C-compounds. Perhaps, C2 has more activity than C1, or can be more related to use with heavy hydrocarbons.

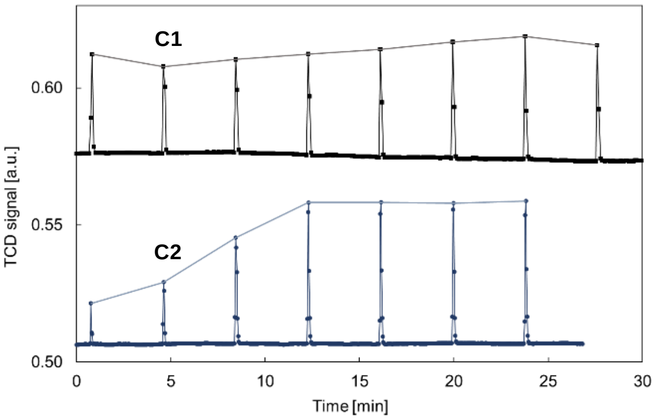

Figure 3: CO pulse for catalysts C1 and C2.

With the previous results, the catalytic materials have been used for thermal catalytic cracking for glycerol, oil and desalted oil. These experiments were conducted with a thermogravimetric analysis-TGA.

3.4 Catalytic activity on the thermal-catalytic cracking of hydrocarbons

The results of catalytic activity with TGA test are shown in the Figure 4 for glycerol (a) and desalted oil (b). For the two hydrocarbons, the experiments were carried out at space-time: 0.15 $g_{catalyst}/g_{HC}$ and prior the experiments the catalysts were reduced in an H_2/He atmosphere because have metallic active sites. Both catalysts were compared with samples in a thermal cracking without a catalyst.

The results can confirm the effect of the reduced catalysts on the thermal cracking of the hydrocarbons, this effect can be observed as much as the weight loss increases in the experiments with the catalysts.

However, the catalysts have a totally different behaviour with both the glycerol (Figure 4a) and the desalted oil (Figure 4b). C2 accelerated the thermal cracking faster than C1 with the glycerol samples, probably due to Cr has more activity for glycerol conversion to light olefins than other metals according to Zakaria et al. (2012).This result is consistent with the capacity for C2 to CO chemisorptions as shown in Figure 3. The content of sulphur can affect the glycerol thermal composition, for this reason, C1 tends to lose less weight compared with the experiment without catalyst.

On the Figure 4b, it is shown the effect on the catalytic thermal decomposition of desalted-oil. In this sample, high temperature for the reaction is needed. Both catalysts promote the weight loss, but C2 promotes more decomposition on the oil than C1. More pore volume and surface area can be related to this result. However, the presence of Fe on the C2 can be the main reason for the best catalytic behaviour, some studies (Sedighi et al., 2013; Li et al., 2010) have showed that the modification with Fe to ZSM-5 zeolites promotes better catalytic activity on the cracking processes.

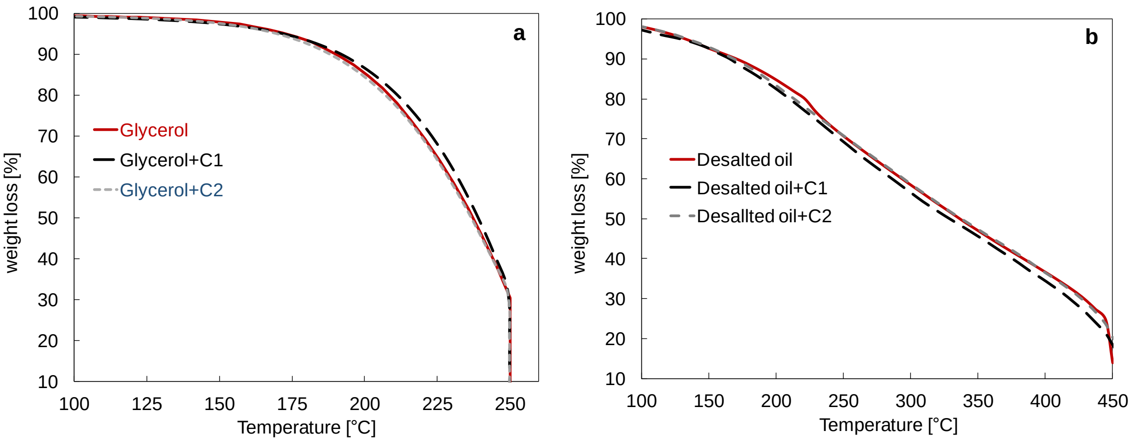

Figure 4: Thermo catalytic cracking of (a) glycerol and (b) desalted oil

All the previous results confirm that the sludge of wastewater treatment from textile industries can be recovered in other products with added value as catalysts which can be used in petrochemical processes.

4. Conclusions

The residual sludge derived from wastewater treatment in the textile industries has metals like Fe and Cr, which can be used as catalytic materials during their reducing phase for the decomposition of hydrocarbons.

Thermal treatment of these sludges is important for the synthesis of the catalyst because when the calcination temperature increases, the surface area, and pore volume decrease.

The calcination process affects the surface properties of the catalyst, because when the surface area becomes smaller there is not warranty of physisorption properties.

The optimum calcination temperature was 600 °C. For C1 the main metal component is Fe and it has a specific area of 30.36 m^2/g and for C2 the metals are Cr and Zn and this material has a specific area of 31.73 m^2/g.

Regarding to the organic content, the existing metals in the active phase and the crystalline structure between C1 and C2, depends on the different chemical substances that the industries use to dye and to obtain different finishes in the textile fibers.

C2 has a notorious capacity of physisorption and chemisorption compared with C1 but both can be used as catalyst thermal cracking of hydrocarbons. C1 has the more catalytic effect on the decomposition of oil due to the Fe content whereas C2 promotes more efficiently the decomposition of glycerol.

The sludges of the textile industry can be valued for this thermal process and can be converted into chemicals with high added value as catalysts.

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