

ELECTRON BEAM APPLICATION FOR REGENERATION OF CATALYSTS USED IN REFINERY CRACKING UNITS

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ABSTRACT

A catalyst is a substance that alters the rate of a reaction. The process of catalysis is essential to the modern day manufacturing industry, mainly in Fluid Catalytic Cracking Process (FCC) units. However, long-term exploitation of oil and gas processing catalysts leads to formation of carbon- and sulfur-containing structures of coke and dense products on the catalyst surface. They block reactive catalyst sites and reduce the catalytic activity. The main advantage of radiation processing by electron beam (EB) and gamma rays is chain cracking reaction in crude oil. Otherwise, under exposure to ionize radiation, considerable structure modification of equilibrium silica-alumina catalyst from FCC process may occur, in addition to the removal of impurities. The conditions applied in the irradiation range (20-150 kGy) of gamma rays and electron beam were not sufficient to alter the structure of the catalyst, whether for removal of the contaminant nickel, a major contaminant of the FCC catalyst, either to rupture of the crystalline structure either for the future reutilization of chemical elements. Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRFS) analysis were used to characterize and evaluate effects of radiation processing on equilibrium catalysts purification. To evaluate and comprehend the reactive catalyst sites, Scanning Electron Microscopy (SEM) and particle size distribution analyses were carried out.

1. INTRODUCTION

The attempts to apply gamma rays irradiation method to fuel processing have been performed for years. Recently, gamma radiation has been proved to be an efficient method to removal thiol-sulfur from the simulated oil, and only several kilogray (kGy) was needed to obtain over 90% of the removal efficiency when some additives were used. The gamma rays irradiation has been found to be able to decompose dibenzothiophene in the simulated petroleum successfully in our previous study. However, the employed irradiation dosage was rather high to allow about 60% of the conversion efficiency [1].

The irradiation would be applied during the process of distillation of petroleum. In this context there is still a very important component in the process may have its effect changed with the irradiation: the catalyst.

In the catalytic cracking process, also known as FCC (Fluid Catalytic Cracking), the load (gas oil from the vacuum distillation and would be used as fuel oil) comes into contact with a catalyst at an elevated temperature, occurring rupture (cracking) of molecular chains, giving rise to a mixture of hydrocarbons which are further fractionated. This process has as main purpose the production of LPG (liquefied petroleum gas) and/or naphtha. Meanwhile, products are formed heavier than naphtha and a high residual carbon content, called coke, which is deposited on the catalyst surface [2].

The ionize radiation impacting the sulfur components would then have a double positive aspect in both the decomposition of the oil components as in the coke deposited on the catalyst.

2. METHODS, MATERIALS AND TESTING PROCEDURES

2.1. Material

The commercial FCC catalyst both virgin and exhausted used in petroleum refineries, which composition is mainly aluminum oxides, silicon oxide and aluminum silicate; nickel nitrate from Impex analytical grade, dichloromethane from Vetec also analytical grade, filter paper Whatman 42 (15 cm) and deionized water. A third sample of catalyst was prepared by contaminating the virgin catalyst with 3,000 ppm of nickel.

2.2. Radiation Processing

The virgin and exhausted catalyst samples were irradiated at room temperature using a Cobalt-60 Multipurpose Gamma Irradiator at absorbed doses of 20 kGy, 50 kGy, 100 kGy and 150 kGy and another batch of contaminated catalyst was irradiated at room temperature using an electron beam accelerator (EBA) Dynamitron DC1500/25/04, model JOB 188 at same doses.

2.3. Chemical Processing

The virgin catalyst was contaminated with 3,000 ppm of nickel following the Mitchell technique [3]. The contaminated batch was heated under reflux with dichloromethane as well as another contaminated batch irradiated with electron beam (20 kGy).

2.4. Analysis

The catalysts were first analyzed by Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) using an Perkin-Elmer Spectrum 100 to compare the

influence of the gamma rays and also the electron beam (EB) effects on the structure of the catalyst.

Virgin, exhausted and after thermal treatment under reflux catalysts were analyzed by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXFRS) using a Shimadzu Co., model Rany 720 spectrometer.

All catalysts were observed with a Scanning Electron Microscope (SEM), model Hitachi Tabletop TM-3000.

3. RESULTS AND DISCUSSION

Nickel and vanadium are the most relevant poisons for catalytic cracking catalysts so the virgin batch was contaminated to understand the irreversible contamination caused by nickel [4].

ATR-FTIR analysis has proved the irradiation with gamma rays on virgin and also exhausted catalysts did not change any molecular structure (Fig. 1 and 2).

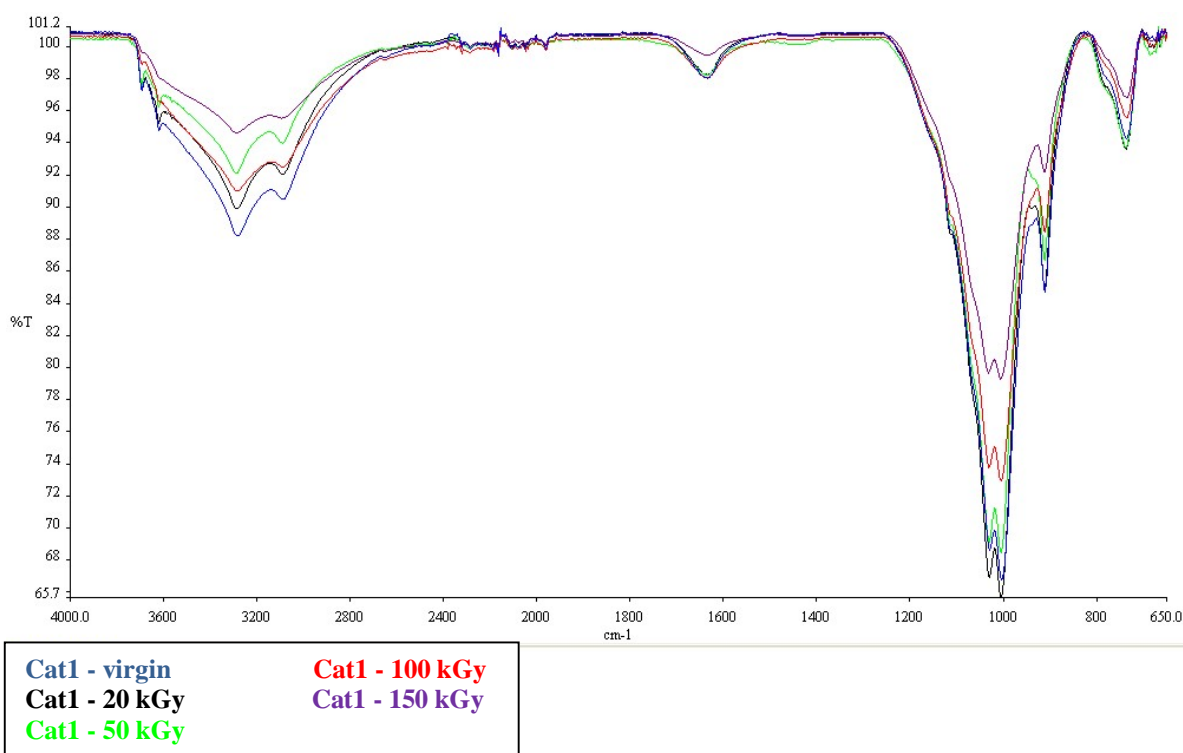


Figure 1: FTIR spectrum of virgin and irradiated virgin catalysts with gamma rays.

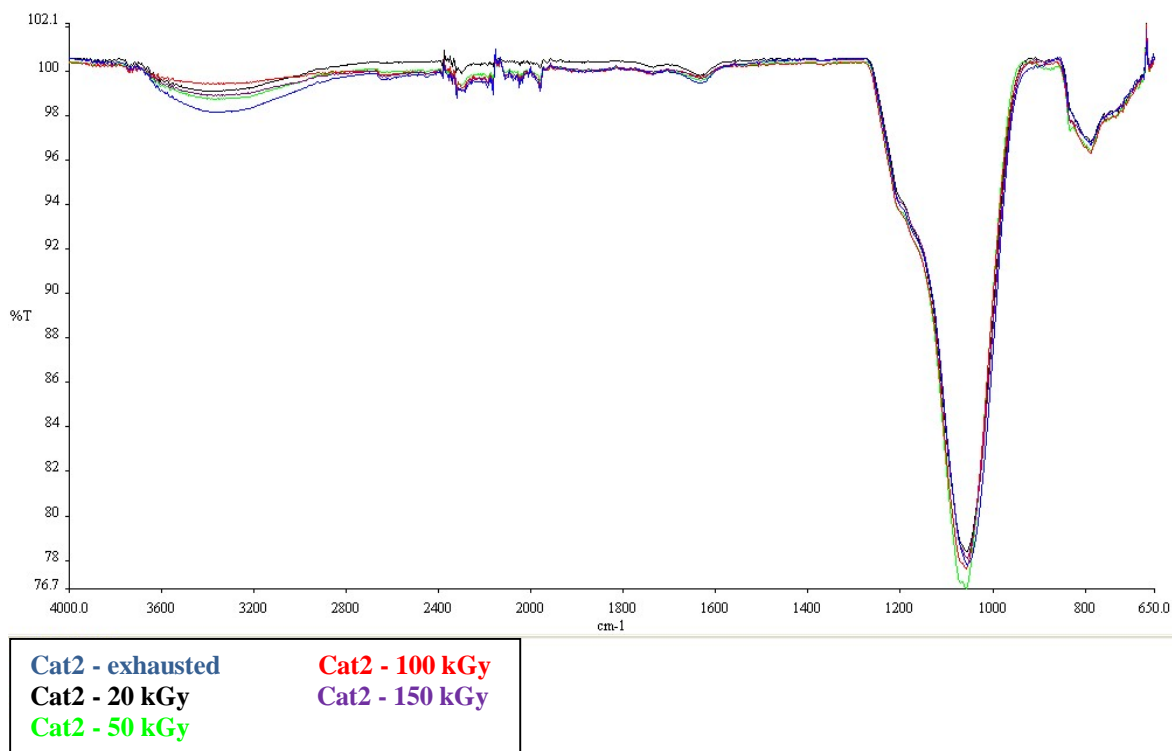


Figure 2: FTIR spectrum of exhausted and irradiated exhausted catalysts with gamma rays.

The technique of Scanning Electron Microscopy (SEM) allows the initial observation of average grain sizes and shape (Fig. 3, 4 and 5).

In Table 1 are shown the average particle sizes of virgin, exhausted, contaminated, contaminated and irradiated, contaminated and filtered catalysts.

Table 1: Catalyst average particle sizes.

Average Particle Sizes (μm)	Min.	Max.
Contaminated catalyst	85	140
Contaminated catalyst and irradiated at 100 kGy (EB)	77	125
Filtered contaminated catalyst	115	140
Contaminated catalyst heated under reflux (3h40min)	95	140
Virgin catalyst	110	140
Exhausted catalyst	75	110

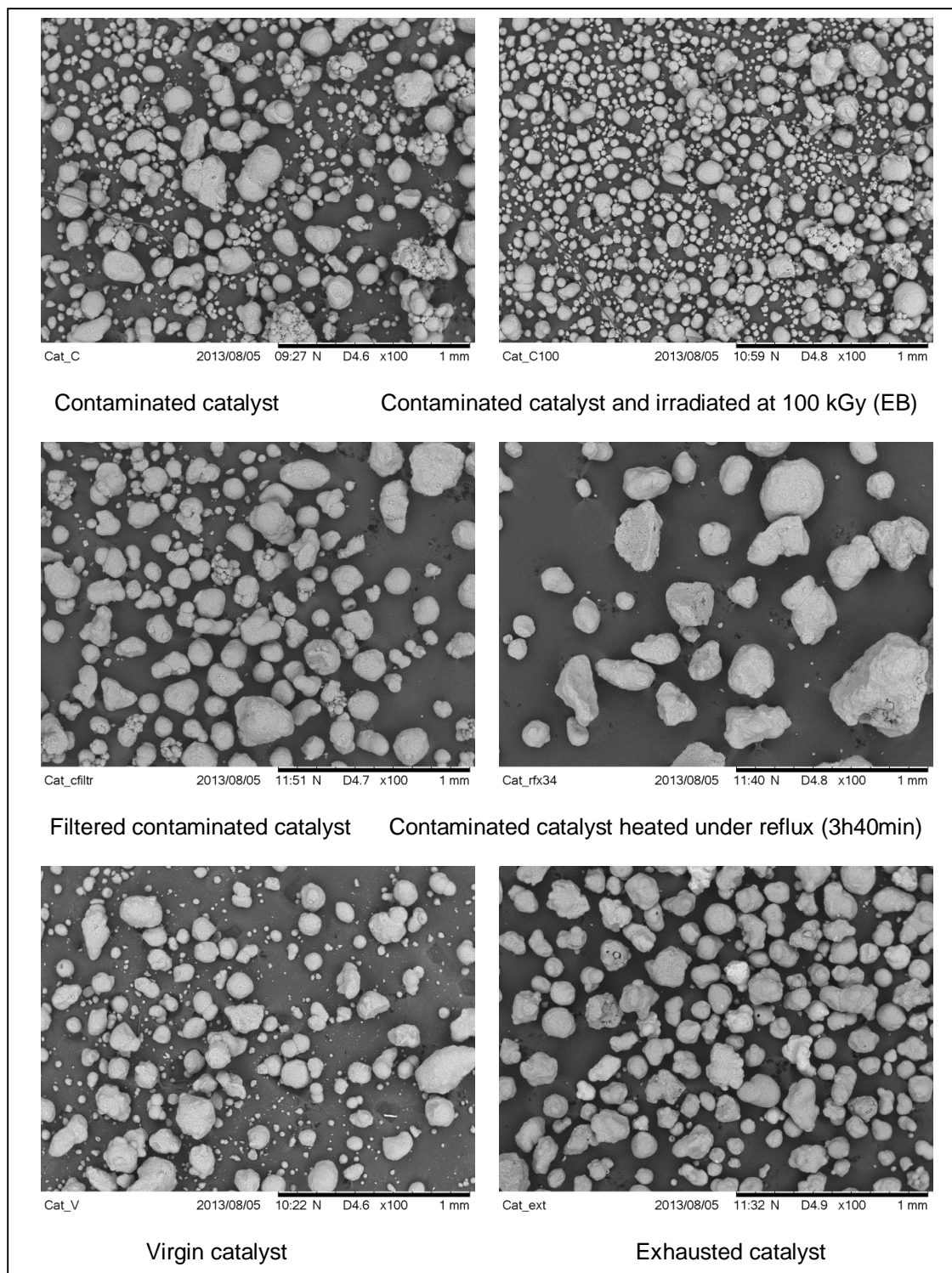


Figure 3: Scanning Electron Microscopy (x100).

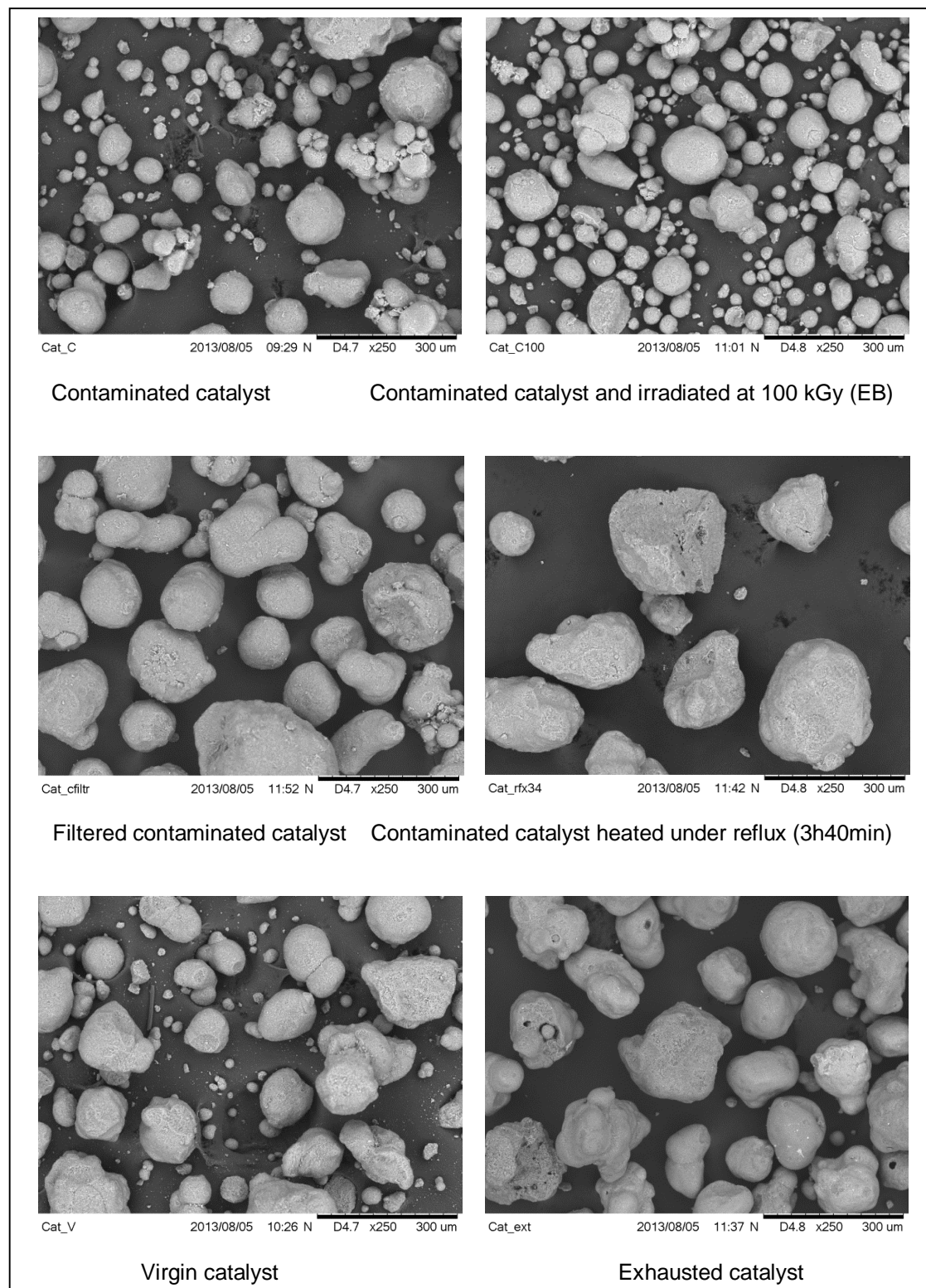


Figure 4: Scanning Electron Microscopy (x250).

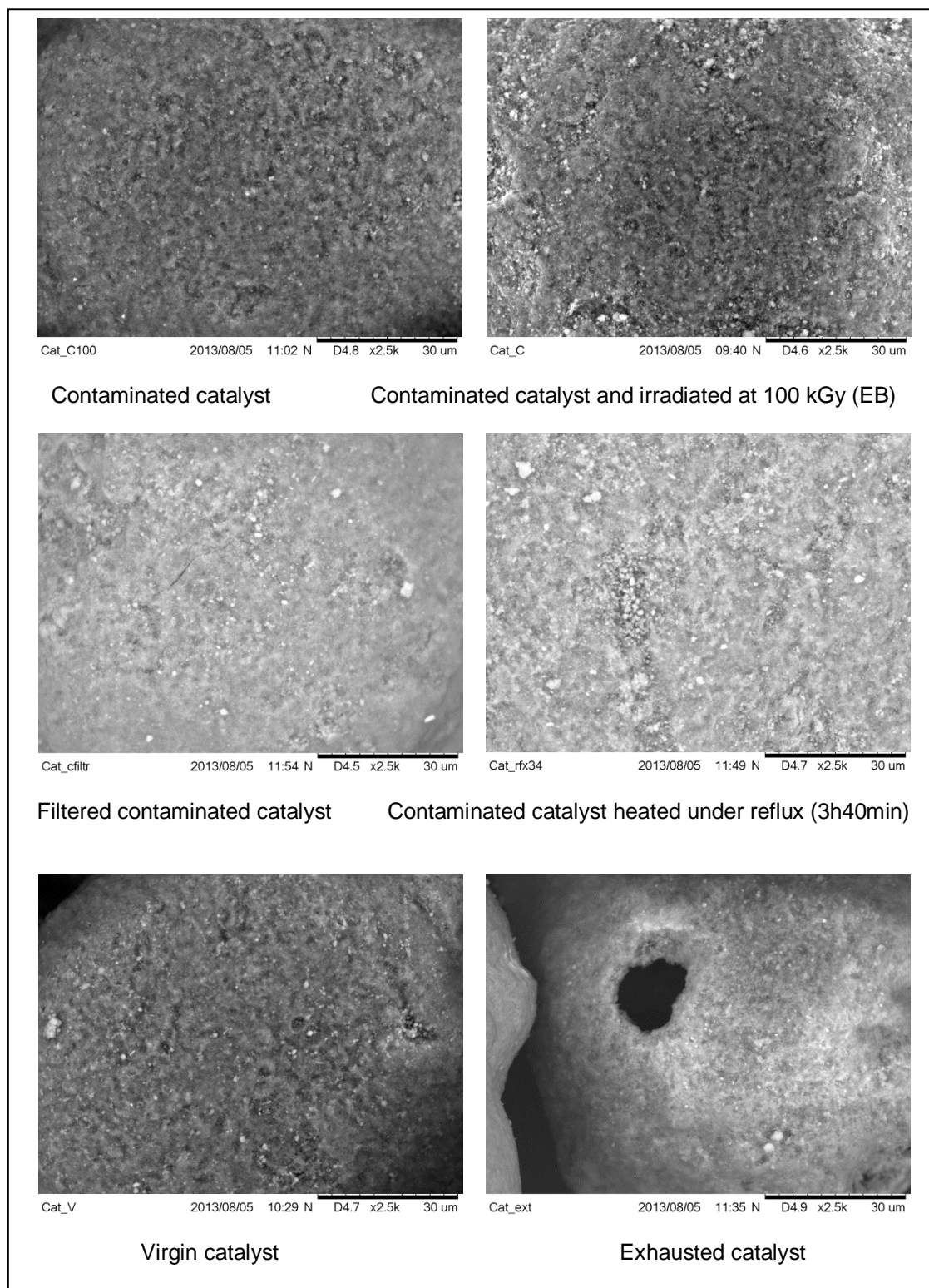


Figure 5: Scanning Electron Microscopy (x2500).

The Scanning Electron Microscopy (Fig. 3, 4 and 5) verified that the catalyst contaminated batches presents larger grains started at the pre-sintering stage due to calcination at high temperatures. It isn't possible to say that electron beam irradiation altered the shape or the average grain size, comparing the images obtained.

Considering all the SEM images, the clearest difference is presented by the exhausted catalyst; it was possible to verify holes and ruptures on the circular forms as well as the reduction of average grain size due the distillation process in refineries.

A batch of contaminated catalyst was washed four times with 20 mL of deionized water and filtered through Whatman 42 (15 cm) filter paper to check if the presence of soluble salts would alter the average grain size. The contaminated catalyst was heated with dichloromethane under reflux for 3 hours and 40 minutes to evaluate the effect of organic solvents in catalyst components. In both cases, the extraction of nickel contaminant was studied.

It was verified by EDXRFS that nickel extraction was made more efficient by washing time with dichloromethane under reflux than with electron beam irradiation treatment.

Elemental determination using the EDXRFS spectrometry was performed at Chemical and Environmental Center (CQMA – IPEN/USP) using a Shimadzu Co., model Rany 720 spectrometer, to understand if the irradiation by electron beam facilitates the removal of contaminating element (nickel), or if irradiation alters the catalyst structure to cause breakage which can be verified after-treatment heating under reflux.

The data obtained as shown in Tables 2, 3 and 4 illustrates that irradiation does not affect the binding of nickel on catalyst and that contaminant can only be released from the catalyst after washing, regarding the structure of the catalyst. It is found that the percentage of elements does not change significantly, indicating that electron beam irradiation does not cause breakage of the catalyst which could be verified by Scanning Electron Microscopy or EDXRFS.

Analyzing the data from the EDXRFS is possible to assert that the nickel contamination was efficient comparing contaminated catalyst and irradiated at 20 kGy (EB) and virgin catalyst (Tables 2 and 3). However, the washing of the catalysts on which irradiated or not, does not have many differences, which becomes different when the washing time changes from 1 hour to 3 hours and 40 minutes. In this aspect the specified irradiation conditions does not alter the yield of purification catalyst.

Table 2: Energy Dispersive X-Ray Fluorescence (EDXRFS) analysis in virgin catalyst versus exhausted catalyst.

Oxide	Virgin catalyst	Exhausted catalyst
%		
Al ₂ O ₃	60.9±0.1	44.8±0.1
SiO ₂	35.3±0.1	47.7±0.2
La ₂ O ₃	2.06±0.03	2.4±0.07
Fe ₂ O ₃	1.04±0.02	0.86±0.01
SO ₃	0.27±0.01	0.18±0.02
K ₂ O	0.185±0.004	0.091±0.010
V ₂ O ₅	0.13±0.01	1.7±0.3
P ₂ O ₅	-	0.58±0.02
CeO ₂	-	0.40±0.03
µg.g ⁻¹		
CaO	235±22	1900±200*
MnO	143±22	58±14
ZrO ₂	103±21	92±21
Ga ₂ O ₃	79±15	63±5
CuO	77±4	82±4
ZnO	57±2	122±7
SrO	39±2	102±5
NiO**	14±7	10400±200**
Sb ₂ O ₃	-	765±53
Rb ₂ O	-	10±2
PbO	-	93±6

Number of repetitions = 3

- Undetectable

* $1870 \pm 240 \text{ µg.g}^{-1} = 0.187 \pm 0.024\%$

** $10370 \pm 200 \text{ µg.g}^{-1} = 1.037 \pm 0.020\%$

Table 3: Energy Dispersive X-Ray Fluorescence (EDXRFS) analysis: contaminated catalyst irradiated at 20 kGy (EB) versus contaminated catalyst treated under dichloromethane reflux (1h).

Oxide	Contaminated catalyst irradiated at 20 kGy (EB)	Contaminated catalyst treated under dichloromethane reflux (1h)
%		
Al ₂ O ₃	60.6±0.3	61.1±0.3
SiO ₂	38.5±0.2	34.8±0.2
La ₂ O ₃	1.43±0.03	1.41±0.03
Fe ₂ O ₃	0.95±0.01	0.93±0.01
TiO ₂	0.87±0.03	0.86±0.03
NiO	0.542±0.006	0.511±0.006
SO ₃	0.262±0.02	0.264±0.02
K ₂ O	0.14±0.01	0.14±0.01
µg.g⁻¹		
CaO	209±50	240±50
ZnO	66±12	73±10
Ga ₂ O ₃	75±10	73±10
ZrO ₂	133±8	104±7
SrO	39±6	31±6

Table 4: Energy Dispersive X-Ray Fluorescence (EDXRFs) analysis: Contaminated catalyst irradiated at 20 kGy (EB) treated under dichloromethane reflux (1h) versus contaminated catalyst treated under dichloromethane reflux (3h40min).

Oxide	Contaminated catalyst irradiated at 20 kGy (EB) treated under dichloromethane reflux (1h)	Contaminated catalyst treated under dichloromethane reflux (3h40min)
%		
Al ₂ O ₃	60.9±0.1	60.9±0.3
SiO ₂	34.8±0.1	35.1±0.1
La ₂ O ₃	1.45±0.03	1.37±0.03
Fe ₂ O ₃	0.94±0.01	0.884±0.01
TiO ₂	0.87±0.02	0.83±0.02
NiO	0.521±0.006	0.492±0.006
SO ₃	0.31±0.01	0.32±0.01
K ₂ O	0.197±0.009	0.15±0.01
µg.g ⁻¹		
CaO	320±60	378±60
ZnO	100±10	98±8
Ga ₂ O ₃	70±4	76±10
ZrO ₂	120±6	70±5
SrO	10±1	26±6

4. CONCLUSION

The conditions applied in the irradiation range (20-150 kGy) of gamma rays and electron beam (EB) were not sufficient to alter the structure of the catalyst, which is demonstrated in ATR-FTIR spectra and verified with Scanning Electron Microscopy.

Using irradiation to facilitate the removal (meaning the catalyst regeneration) of nickel contaminant, a major contaminant of the FCC catalyst, whether to rupture the crystalline structure (meaning the future reutilization of chemical elements present in the catalyst) isn't possible in those irradiation conditions, as the EDXFRS data presents.

The EDXFRS analysis also gives important information about the transformation that occurs in virgin catalyst after used (exhausted) in refineries, it is possible to assert that some aluminum molecules is lost during the process, when the percentage about 61% reach about 45% the catalyst is considered exhausted, while other contaminants blocks reactive catalyst sites as well as damages in it structure.

However, in view of these conditions, some authors have used irradiation for chain cracking reaction [5,6]. Then, one beneficial factor is the understanding that irradiation in crude oil context does not affect the catalyst structure, which could be used in refineries without interfering the catalyst performance.

5. SUGGESTIONS FOR FUTURE WORKS

Ni(Co)-Mo/Al₂O₃ catalyst is also used in the crude-oil processing, in a stage called Hydrocatalytic Cracking (HCC), the presence of Molybdenum and Cobalt adds high value to the catalyst.

The use of Ni(Co)-Mo/Al₂O₃ catalyst is an example of material that, after thoroughly characterized, became framed as hazardous waste from the late 90's. This situation was maintained in the review published by the Environmental Protection Agency (EPA) in September, 2004 [7].

When studying electron beam (EB) with higher energies is possible to induce the decomposition of supported Ni(Co)-Mo/Al₂O₃ sulfide catalyst and organic fragments of hydrogenation catalyst wastes and also recovery noble materials such as cobalt and molybdenum [8], as well as, the study of catalyst impregnated with coke from the crude oil distillation on an industrial scale.

To evaluate and comprehend the crystalline structures of Ni(Co)-Mo/Al₂O₃ and also FCC catalysts after gamma rays and electron beam irradiation, it will be necessary to carry out X-Ray Diffraction (XRD).

For the FCC catalyst a feasibility study will be made to understand if the extraction of silica or an addition of aluminum would alter the reactivity of the exhausted catalyst once the percentage of aluminum and silica reaches the virgin percentage.

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