Deposits Effects on Catalysts Porous Structure and Chemical Activity during Residuum Catalytic Hydro-treatment

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Abstract Catalyst Porous structure parameters and activity were investigated during the catalytic hydro-treatment of Heavy Arabian Oil atmospheric residuum utilizing a fixed bed catalytic reactor with recycle. Two model Hydro-treating catalysts CAT-1 containing 0.5 wt% Molecular Sieves (MS) 13X, and CAT-2, having different physical and chemical properties were used in this investigation. Spent, extracted and dried, catalyst samples were analyzed for their physical features and chemical deposits for both types, CAT-1 and CAT-2, with sizes having (L_{p0}) = 0.059 mm and $\overline{Lp_1}$ = 0.326 mm. It was found that carbonaceous deposits on CAT-1, $\overline{Lp_0}$ = 0.059 mm approached 41.91 wt% (S, C, H and N) g/100 g regen. Cat.. The porous structure parameters were affected by the deposited materials. Surface areas lost due to deposits were in the range of 45 to 55% and pore volumes decrease was in the range of 43 to 52% compared with the fresh samples. Probable pore diameters decreased from around 80 Å to 43 Å. Pores in the range between 105 to 165 Å disappeared Especially in CAT-1 samples. Coke content of S, C, H, and N with respect to the weight of the regenerated catalyst was around 4.0, 34.0, 1.9 and 0.50 wt. % respectively. Vanadium (V) and Nickle (Ni) contents were in the range 0.63 and 0.27 wt. % respectively. Extracted and dried spent catalysts samples were oxidized with dry air stream at 380°C. Upon regeneration the carbonaceous deposits were removed and the porous structure parameters were recovered up to levels approaching 79-89% of those recorded for the fresh samples, depending on their sizes.

Keywords Catalyst, Pore Structure, Deposits, Regeneration, Residuum, Metals

1. Introduction

It has been suggested that the operating catalyst

behavior is drastically affected by the physicochemical properties of the treated oil feedstock and the catalyst characteristics [1, 2]. The analysis of used catalysts led to that the activity loss is attributed to carbonaceous and metallic deposits altering the chemically active surface and the physical structure of the employed catalyst [3,4]. The contribution of these factors depends on the reaction conditions, the origin of the feed stocks, the desired degree of Hydro-treatment and finally on the catalyst physicochemical features [5, 6].

1.1. Coke Deposition and Properties

Coke deposition within the catalyst structure is one of the factors imposing intra-particle diffusion limitations to both reactant and product molecules either by partial or complete pore plugging mechanism [7]. Furthermore, coke containing N-O heteroatoms affect catalyst activity poisoning acidic active sites [8,9]. It is also accepted that coke develops from reactive, unstable hydrocarbon species (coke precursors) with small or large molecular sizes (resins, heterocyclic compounds and Asphaltenes) [10,11,12].

1.2. Metal Deposits

At the time where the effect of coke deposits is limited to reversible modifications of the pore structure, the effect of metallic deposits is responsible for the permanent alteration of the physical and chemical characteristics and are considered as the most critical factors determining catalyst life self, because they are irreversibly adsorbed on the catalyst active surface.

A controlled oxidation of spent catalysts can remove the deposited carbonaceous materials. Nickle and Vanadium are the most important metallic elements that affect catalyst activity and are frequently present in petroleum crudes. Porphyrins, Asphaltenes and Resins are

believed to be the main source of metallic sulfides deposited on the operating catalysts [1,3,11].

1.3. Chemical Behavior of Catalysts during Oil Hydro-Treatment

It is believed that the stable and active catalyst species are the sulfided metals i.e. Mo_xS_y and Co_zS_d . As it is impossible to get reliable composition data on operating industrial catalysts in situ, it was mentioned that for oxidic precursors treated with ($\text{H}_2/\text{H}_2\text{S}$) at 400°C the degree of sulfidation was 95%, with (S/Mo) atomic ratio approaching 2.44, and (S/Co) atomic ratio around 0.63 [13].

1.4 Quantitative Determination of Coke Deposited on Hydro Treating Catalysts

The evaluation of the real effect of the carbonaceous materials upon the pore structure and the intrinsic chemical activity of the active catalyst phase (in situ) requires a standard method of coke and metal determination. Ammus [3] concluded that there is no standard method for quantitative determination of coke. Operating Hydro-treating catalysts on discharge they may contain unreacted oil, oil products, intermediate compounds, coke and metallic deposits mainly V and Ni. Deactivation of catalysts and selectivity alteration can be attributed to coke and metal deposits plugging pores containing active surface area.

Reliable determination of coke requires de-oiling of the (as discharged) used catalysts to remove oily substance and an accurate determination of the metal deposits. It was suggested by Ammus and Androustopoulos [6], that the most effective and useful method of de-oiling is the benzene extraction. Coke evaluated by subtracting the weight of the oxidized catalyst from the extracted and dried used catalyst is erroneous, because coke evaluations must contain a correction factor for the conversion of sulfides to the oxides of the active constituents. Thus coke must be expressed per mass of sulfide form of catalyst and sulfide metal deposits. The suggested form of coke and metal deposits bears a physical significance and is based on the assumption that both complete sulfidation and oxidation of the respective catalyst had occurred, so a reduced error is anticipated.

2. Experimental

Two model catalyst CAT -1 and CAT -2 with different physical and chemical features [Table 1] were investigated by Amous [14], applying Particles with different characteristic lengths $\bar{L}p_0=0.059\text{mm}$ and $\bar{L}p_1=0.326\text{ mm}$. The properties of the feedstocks being Hydro-treated are depicted in Table 2 [14]. CAT-1 with $\bar{L}p_0=0.059\text{ mm}$ containing 0.5 wt.% (MS 13X) is utilized

in a plug flow reactor operating with high recycle ratio (complete back mixing at) 350°C , 50 atm. and a LHSV of 2.6 h^{-1} .

Table 1. Fresh catalysts chemical composition and main pore structure specifications.

Cat.symb.	CAT- 1	CAT- 2
$\gamma\text{-Al}_2\text{O}_3$, Wt%	85.9	86.4
CoO, wt %	3	3
MoO ₃ , wt%	10.6	10.6
MS 13X, wt%	0.5	0
Sg,m ² /g [BET]	188	181
Sg,m ² /g [MP]	114	111
Vp(1)	0.41	0.39
Vp(2)	0.32	0.34
dp(1)	83	87
dp(2)	123	128
pobs.bed,g/cm ³	0.78	0.75

Sg: Specific Surface Area / BET. [m²/g], M.P**: Mercury Penetration(1800 bar), Vp⁽¹⁾: Pore volume measured with N₂ Ads-Des technique, Vp⁽²⁾: Pore volume measured with mercury penetration, dp⁽¹⁾: Most probable pore diameter in Angstrom(Å) measured with N₂ Ads-Des., dp⁽²⁾: Most probable pore diameter in Angstrom(Å) measured with mercury penetration technique. $\rho_{\text{obs.bed}}$ Observed bed density g/cm³.

Table 2. Properties of Treated Heavy Oil Residuum

Property	Value
Boiling point, °C	>330°C
API	9.0
S, %wt	4.65
V+Ni, ppm	132
Carbon residue, %wt	13.62
Sp. gravity, 15/4 °C, g/cm ³	1.007
Kinematic viscosity, 122°F, cSt	229

Porous structure parameters are measured applying the N₂ adsorption –desorption and Mercury penetration techniques and specific surface areas, pore volumes and pores diameters and pore size distributions were deduced for fresh, spent and regenerated catalyst samples.

Catalyst activity is investigated as a function of catalyst age. The reactor operating 10 hours a day in a steady state operation was let to operate for 45 days. The attained conversion of sulfur X_{f0} is measured for fresh catalyst, and then the conversion of sulfur X_{fi} is determined every day (run) for the following 45 days. The ratio X_{fi}/X_{f0} vs. catalyst age is used to express relative activity diminution. The observed values of X_{fi}/X_{f0} vs. catalyst age are shown [Table 3, 4].

3. Results and Discussion

It can be seen from Table 3, that (CAT-1, $\bar{L}p_0=0.059\text{ mm}$) activity increases very slightly during the first

100-200 hours and begins to decrease later and drops to about 80% of the original value after 45 days which means that each cm^3_{cat} had treated 296.1 cm^3 oil.

Table 3. Chemical conversion attained vs. Catalyst age, $\text{ML}_{\text{oil}}/\text{cm}^3_{\text{cat}}$.

Catalyst age $\text{ML}_{\text{oil}}/\text{cm}^3_{\text{cat}}$ (10 hours daily)	Working time, days	Sulfur content, S wt%	X_f %	Relative activity = X/X_0
6.6	1	2.35	49.46	1
65.8	10	2.3	50.54	1.022
98.7	15	2.34	49.68	1.004
131.6	20	2.37	49.03	0.991
164.5	25	2.45	47.31	0.957
197.3	30	2.52	45.81	0.926
230.2	35	2.55	45.23	0.914
263.2	40	2.6	44.04	0.89
296.1	45	2.8	39.78	0.804

Disposed catalyst particles with $\overline{Lp}_0=0.59\text{mm}$ after 450 hours of operation are washed and extracted with Octane for one hour at 125°C to remove soluble constituents, and then the extracted samples were dried at 128°C under vacuum of 600 mmHg to remove all the absorbed soluble and other absorbed traces if any. Extraction with Octane cannot scrape and extract light coke deposited in the pore structure of the spent catalyst compared with Benzene which has a higher solubilizing ability to light coke depositions.

The porous structures of the dried and extracted spent catalyst particles are investigated and pore structure properties for pulverized CAT-1 and CAT-2 particles determined are shown in [Table 5]. Drying is followed by a controlled oxidation with air at 380°C for 3 hours to assure that the weight of the oxidized sample had reached a constant value. The decrease in the weight of the spent catalyst due to oxidation is calculated and the weight loss

Divided by the weight of the oxidized catalyst is considered as the weight percentage of coke deposited during the 450 hours of operation.

Table 4. Chemical conversion attained vs. Catalyst age, $\text{ML}_{\text{oil}}/\text{cm}^3_{\text{cat}}$.

Catalyst age $\text{ML}_{\text{oil}}/\text{cm}^3_{\text{cat}}$ (10 hours daily)	Working time, days	Sulfur content, S wt.%	X_f %	Relative activity = X_f/X_0
6.6	1	2.51	46.02	1
65.8	10	2.46	47.11	1.024
98.7	15	2.46	47.12	1.024
131.6	20	2.46	47.03	1.02
164.5	25	2.55	45.12	0.98
197.3	30	2.54	45.41	0.986
230.2	35	2.56	45.05	0.979
263.2	40	2.65	43.04	0.9352
296.1	45	2.74	41.09	0.893

The analysis showed that the S, C, H, N contents of the coke were around 3.96, 35.96, 1.88, 0.49 wt. % respectively. The metallic deposits were 0.61 and 0.27 wt. % for Vanadium and Nickle respectively for

CAT-1 sample, $\overline{Lp}_0=0.59\text{mm}$, while those for CAT-2 sample $\overline{Lp}_0=0.059 \text{ mm}$ contained 3.43, 28.7, 3.61 and 0.38 wt. % S, C, H and N respectively. Vanadium and Nickle contents of the deposits were found to be 0.46 and 0.23 wt. % as is shown in Table 6.

The higher levels of deposits noticed for CAT-1 may be attributed to the molecular sieves MS 13X with their active surface converting the high molecular weight molecules

Embedded with C, N, V, and Ni as Asphaltenes and Resins present in heavy oil fractions.

Illustrating these results, each 1 gram of spent CAT-1 loses 0.4097 grams as oxidative coke on burning with air, among those 0.4097 grams 0.0234 g rams are for sulfur, the Remaining weight of the catalyst i.e. 0.5903 grams are considered as regenerated catalyst(including metallic deposits). Hence the S wt. %, $\{^g_s / 100 \text{ g}_{\text{reg.cat.}}\}$ is equal to $0.0234 \text{ g}_s / 0.5903 \text{ g}_{\text{reg.cat.}} = 3.96 \text{ wt. \%}$. The pore structure properties of both catalyst types after regeneration are shown in Table 7.

It is seen that the regeneration released most of the lost pore structure properties, [Table 7].

It is noticed that spent catalysts after 450 hours of operation had lost the major portion of their porous structure parameters, while keeping more than 80% and 89% of their chemical activity for CAT-1 and CAT-2 respectively [14].

Table 5. Spent catalysts pore structure specifications after 450 hours at 350°C , 50 atm., and LHSV 2.6 h^{-1} .

Cat.symb.	Fresh CAT- 1	Spent CAT- 1	Fresh CAT- 2	Spent CAT-2
$\text{Sg}, \text{m}^2/\text{g}$ [BET]	188	85	181	99
$\text{Sg}, \text{m}^2/\text{g}$ [MP]	114	53	111	64
$V_p^{(1)}$	0.41	0.18	0.39	0.23
$V_p^{(2)}$	0.32	0.14	0.34	0.17
$dp^{(1)}$	83	45	87	51
$dp^{(2)}$	123	75	128	82
$\rho_{\text{obs.bed}}, \text{g}/\text{cm}^3$	0.78	0.84	0.75	0.79

The only explanation for this phenomenon is that coke deposited in the pores of the catalysts during the first stages does not impose the active centers to operate as active sites attracting reactants i.e. electrical charges can move through the deposited coke layer and hence catalyzing reactions. As time is increasing metals deposits destroying the active sites either isolating or poisoning them increase and the coke layer becomes more thick and more solid to a degree that electrical charges cannot be interchanged between reacting molecules and so the covered active centers cannot do their assigned job and thus no catalytic activity is observed.

These solid and thick coke layers start to build up after 200 to 300 hundred hours of operation in conjunction with the metallic deposits destroy progressively the catalytic activity of the active

Centers and then causing activity to decreas

progressively. Also the degradation of pore structure parameters observed for CAT-1 and CAT-2 justifies the activity loss observed for both catalyst samples with $\bar{Lp}_0=0.59$ mm, which is found to be 20 and 11% respectively [14].

The analysis of the porous structure of spent CAT-1 and CAT-2 showed that the most probable diameters of pores had dropped to 45 and 51 (Å) for $dp^{(1)}$ and to 75 and 82 (Å) for $dp^{(2)}$ for both samples respectively.

Table 6. Composition of deposits on CAT-1 and CAT-2 samples, $\bar{Lp}_0=0.59$ mm, 450 hours of operation.

Quantity	CAT-1	CAT-2
Weight loss due to oxidation/100 g. spent catalyst sample, %	40.97	37.08
Wight of regenerated cat. Sample, %	59.03	62.92
S wt.%, $g_s / 100g_{reg.cat}$	3.96	3.43
C wt.%, $g_c / 100g_{reg.cat}$	35.58	28.70
H wt.%, $g_H / 100g_{reg.cat}$	1.88	3.61
N wt.%, $g_N / 100g_{reg.cat}$	0.49	0.38
V wt.%, $g_v / 100g_{reg.cat}$	0.61	0.46
Ni wt.%, $g_{Ni} / 100g_{reg.cat}$	0.27	0.23

The micro-pores with diameters less than 20 Angstrom (Å) were seriously infected and isolated. It is believed that the presence of MS-13X with their acidic surface chemistry support the hydrocracking reaction of the heavy molecules like Asphaltenes, resins, etc. Hydrocracking of these large molecules penetrated into the miso and micro-pores causing these to be plugged and hence, isolated in a manner that they could not be able to catalyze the reactions assigned to. The differential pore size distribution of fresh CAT-1 is shown in Figure 1.

The differential pore size distribution of a spent CAT-1 sample used for 450 hours is shown in Fig.2, where most of the miso-pores with dimeters between 80 and 160(Å) had already disappeared. The major portion of the specific surface area and pore volume were lost, [Table 5].

On regeneration, most of the specific surface area and pore volume of the CAT-1 sample were recovered, Table 7.

The differential pore size distribution of regenerated CAT-1 samples is shown in Fig. 3, with a probable pore diameter around 57 (Å).

The pore size distributions for both fresh and spent CAT-2catalysts are shown in Figures 4 and 5.

On regeneration CAT-2 sample recovered 95% of the Sg [BET] and 94.4% of the Sg [MP]. The probable pore diameter recovered 74% of its original value determined value for fresh sample in the miso-pore size region and 95% of the original value for probable pore diameter determined for macro pores sizes, [Table 7]. The

differential pore size distribution is shown in Fig. 6.

Table 7. Pore structure parameters of regenerated catalysts

Cat.symb.	Regenerated CAT- 1	% recovery	Regenerated CAT-2	% recovered
Sg,m ² /g [BET]	168	89.5	171	95
Sg,m ² /g [MP]	102	90.3	105	94.4
Vp ⁽¹⁾	0.37	89.5	0.37	95
Vp ⁽²⁾	031	95.3	0.32	93
dp ⁽¹⁾ , (Å)	57	68.7	65	74
dp ⁽²⁾ , (Å)	115	93.5	122	95.3

Figure 1. Differential pore size distribution of fresh CAT-1, $\bar{Lp}_0=0.059$ mm.

Figure 2. Differential pore size distribution of spent CAT-1, $\bar{Lp}_0=0.059$ mm

Figure 3. Differential pore size distribution of regenerated CAT-1 sample.

Figure 4. Differential pore size distribution of fresh CAT-2. $\bar{Lp}_0=0.059\text{mm}$

Figure 5. Differential pore size distribution of spent CAT-2. $\bar{Lp}_0=0.059\text{mm}$

Figure 6. Differential pore size distribution of regenerated CAT-2 sample.

Samples with larger particle having $\bar{Lp}_1=0.326\text{ mm}$ showed the results given in Table 8. The spent catalyst samples showed a higher loss in their pore structure parameters [Tables 8, 9].

It can be seen that the modifications in the pore structure of the cylindrical pellets is more severe than that observed for pulverized ones, where surface areas in the miso-pore and micro pore region had lost more than 60 and 54% for both CAT-1 and CAT -2 samples, while miso and macro

pore surface areas lost were 62.5 and 55.7 % for both types. Pore volumes lost as deduced from Tables 8 and 9 are 56.8 and 52.7 % for the miso-pores and 58.6 and 55% for the macro pores region for CAT-1 and CAT-2 respectively. These results may give the explanation of the higher catalytic activity drop observed for catalyst CAT-1 impregnated with MS 13X compared to the decrease in activity drop for CAT- 2. All catalyst Samples, having the same particle size $\bar{Lp}_1=0.326\text{ mm}$, treated with Hydrogen at 300°C and 50 atm. Hydrogen flow rate of 5700 ml/ h, (NTP). Sulfided in situ with feedstocks, $C_{S0}=14.633 \cdot 10^{-4}\text{ g-mol S/cm}^3_{\text{oil}}$, $\text{API}=9$. These samples were used in a fixed bed reactor ($D_{\text{in}} 15\text{ mm}$, Length 230 mm, bed volume 38 cm^3) operating with high recycle ratio (complete back-mixing), $\text{LHSV}=2.6\text{h}^{-1}$, $P=50\text{ atm.}$, $T=350^\circ\text{C}$, initial sulfur concentration $C_{S0}=14.633 \cdot 10^{-4}\text{ g-mol S/cm}^3_{\text{oil}}$, $\text{API}=9$ and $\bar{Lp}_1=0.326\text{ mm}$. [14].

Table 8. Pore structure parameters of fresh catalyst samples. $\bar{Lp}_1=0.326\text{ mm}$

Cat. Sample, $\bar{Lp}_1=0.326\text{ mm}$	Sg [BET], m^2/g	Sg [MP], m^2/g	$Vp^{(1)}\text{ cm}^3/\text{g}$	$Vp^{(2)}\text{ cm}^3/\text{g}$	$dp^{(1)} (\text{Å})$	$dp^{(2)} (\text{Å})$
CAT-1	189.4	115.8	0.406	0.29	77	118
CAT-2	181.3	111.5	.402	0.30	81	122

Table 9. Pore structure parameters of spent catalyst samples. $\bar{Lp}_1=0.326\text{ mm}$, 450 hours of operation.

Cat. Sample, $\bar{Lp}_1=0.326\text{ mm}$	Sg [BET], m^2/g	Sg [MP], m^2/g	$Vp^{(1)}\text{ cm}^3/\text{g}$	$Vp^{(2)}\text{ cm}^3/\text{g}$	$dp^{(1)} (\text{Å})$	$dp^{(2)} (\text{Å})$
CAT-1	75	44	0.18	0.12	38	69
CAT-2	83	49	0.19	0.13	44	73

The degradation of catalyst activity is measured for both catalyst samples particles by measuring the attained chemical conversion versus catalyst age. The experimental results are shown in Table 10 and Table 11 for CAT-1 and CAT-2 respectively. The graphical presentations are shown in shown in Figures 7 and 8.respectively.

The CAT-1 activity data showed that the effectiveness factor $\eta_0=0.940$ for $\bar{Lp}_0=0.059\text{mm}$ and $\eta_1=0.452$ for $\bar{Lp}_1=0.326\text{ mm}$. [14].

The decrease in the activity started early during the initial hours of operation and continued progressively with increasing time, these results showed that during the 450 hours of operation the catalyst had lost 55.41% of its activity. The value of 20 % activity loss calculated for the pulverized particles [14] for the same period of operation, when compared to the 55.41% determined for the

Cylindrical particles, $\bar{Lp}_1=0.326\text{ mm}$, can be attributed to the deposition of coke and metals, a phenomenon which is accelerated by the presence of molecular sieves with their acidic surface supporting the hydro cracking reaction in the outer surface of particles isolating the central and major part of the particle from contributing in the reactions involved.

Figure 7. CAT-1 activity expressed as chemical conversion of sulfur compounds vs. catalyst operating time, ML oil/cm³ catalyst, $\bar{Lp}_1 = 0.326$ mm.

Table 10. Chemical conversion attained vs. Catalyst age, ML_{oil}/cm³ cat., CAT-1 sample. $\bar{Lp}_1 = 0.326$ mm

Catalyst age ML _{oil} /cm ³ cat (10 hours daily)	Working time, days	Sulfur content, S wt. %	X _f %
6.6	1	3.611	22.340
65.8	10	3.70	20.418
98.7	15	3.79	18.430
131.6	20	3.85	17.130
164.5	25	3.94	15.360
197.3	30	4.03	13.340
230.2	35	4.09	12.020
263.2	40	4.14	10.890
296.1	45	4.187	9.960

The activity of CAT-2 sample was investigated at the same operating conditions applied for CAT-1 sample; the results are shown in Table 11 and presented in Fig. 8. The investigation showed that the effects of intra-pellet mass transfer limitations were less severe than those observed for CAT-1 sample.

Table 11. Chemical conversion attained vs. Catalyst age, ML_{oil}/cm³ cat., CAT-2 sample. $\bar{Lp}_1 = 0.326$ mm.

Catalyst age MLoil /cm ³ cat (10 hours daily)	Working time, days	Sulfur content, S wt. %	X _f %
6.6	1	3.63	22.04
65.8	10	3.68	20.78
98.7	15	3.77	18.85
131.6	20	3.83	17.48
164.5	25	3.90	16.09
197.3	30	3.98	14.37
230.2	35	4.04	12.93
263.2	40	4.11	11.52
296.1	45	4.15	10.86

Figure 8. CAT-2 activity expressed as chemical conversion of sulfur compounds vs. catalyst operating time, ML oil/cm³ catalyst, $\bar{Lp}_1 = 0.326$ mm.

The pore structure of CAT-2 sample which is embedded with more pore sizes in the miso- and macro-pores gave it more resistant to the harmful effects of deposits and gave CAT-2 a higher effectiveness factor, $\eta_0 = 0.965$ for $\bar{Lp}_0 = 0.059$ mm and $\eta_1 = 0.479$ for $\bar{Lp}_1 = 0.326$ mm.

The results of the analysis of deposited materials on both catalysts are shown in table 12.

Table 12. Deposits composition on catalyst cylindrical extrudates.

Catalyst samples, $\bar{Lp}_1 = 0.326$ mm	Coke wt. % [#]	V* Wt. %	Ni** Wt. %	Reg. cat. *** Wt. %
CAT-1	30.06	0.402	0.177	69.94
CAT-2	32.65	0.382	0.169	67.35

#: Weight loss due to oxidation/100 g. spent catalyst sample, *: V wt. %, g_v / 100g reg. cat, **: Ni wt. %, g_{Ni} / 100g reg. cat, ***: weight of regenerated catalyst sample/100 g of spent catalyst sample.

On regeneration, both catalysts recovered most of their pore structure parameters. The results are illustrated in Table 13

Table 13. Pore structure parameters of regenerated catalyst samples.

Catalyst	CAT -1	CAT-2
Sg [BET], m ² /g	166.76	163.27
Sg [MP], m ² /g	94.96	99.54
V _p ⁽¹⁾ , cm ³ /g	0.33	0.34
V _p ⁽²⁾ , cm ³ /g	0.21	0.24
dp ⁽¹⁾ , (Å)	54	61
dp ⁽²⁾ , (Å)	96	107

It is clearly noticed that by oxidation of spent catalyst samples the recovery of the specific surface area miso- and micro- pores approached 90%, while the level of recovery in macro and miso-pores was between 80 and 89%. The most probable pore diameter recovered 70 to 75 % of that value measured for fresh samples.

4. Conclusions

The tested catalyst samples lost the major portion of their specific surface area and pore volume on operation. The analyzed deposits contained C, S, N, H, V and Ni. The pulverized samples with $\overline{Lp}_0=0.059\text{mm}$, maintained more than 80% of their activity in spite that more than 60% of their pore surface area and pore volume. CAT-2 with more miso and macro-pores showed to be more resistant to deposits than the CAT-1 embedded with molecular sieves MS 13 X and with more pores in the micro and miso-pores region.

Coke deposited is of changing nature and chemistry. Activity curves and the literature on coke deposition phenomena, support that coke formed in the early stages do not impose active sites from contribution in the catalysis of the reaction assigned to. While as time is increased the coke changes chemistry and nature and begins to hinder the contribution of the active sites side by side with the metallic deposits mainly V and Ni. The larger catalyst particles with $\overline{Lp}_1=0.326\text{ mm}$ showed a higher rate of catalyst deactivation, where activity diminution curves showed higher deactivation rates compared with the smaller pulverized ones.

Intra-particle mass transfer limitations were obvious and their effects were clear and influential especially for the particles with $\overline{Lp}_1=0.326\text{ mm}$, where η was 0.452 and 0.479 for CAT-1 and CAT-2 respectively. The amounts deposited support that the external part of the particles was exposed to the metallic and coke deposits.

Finally on regeneration the major portion of pore structure parameters were recovered and a small portion remained unrecovered.

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