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Properties Analysis of Spent Catalyst for Fixed-Bed Residue Hydrotreating Unit: Composition of Deposited Elements Along Catalyst Bed

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Abstract

Element compositions of spent catalyst from a commercial fixed-bed residue hydrotreating unit of Petro-China were analyzed in order to investigate the reasons for the catalyst deactivation. The spent catalysts were sampled from different axial position of the reactor. Depositions of C, H, S, N, Ni and V on the spent catalysts were studied. No necessary relation was observed for the contents of various deposited elements along the bed at the end of a run. The deposition amount of elements was mainly related to local reaction conditions and catalyst loading states in the fixed-bed. The catalysts with high metal depositions have low contents of coke, high contents of sulfur and high H/C, which indicates that residue hydrotreating is an autocatalytic process. Metal sulfides deposited on catalysts have a hydrogenation activity in residue hydrotreating. The coke on residue hydrotreating catalysts mainly comes from some specific condensed ring structures containing nitrogen existed in asphaltene which is difficult to hydrotreat.

Key words: Spent catalyst; Residue hydrotreating; Deposited elements; Composition

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INTRODUCTION

The chemical composition of residue is very complicated which contains different kinds of hydrocarbons, non-hydrocarbons and organometallic compounds. In principle, all the elements in residue have a possibility to deposit on catalyst in hydrotreating. So, it is very difficult to analyze the element composition of spent residue hydrotreating catalyst in detail because of the heavy workload. Considering the element contents in residue and their effect on catalyst properties, our research mainly analyzed the deposition of elements such as C, H, S, N, V and Ni on catalysts which were obtained from different axial positions of an industrial fixed-bed residue hydrotreating reactor. The composition and structure changes of catalyst were studied to discover the deactivation reasons of residue hydrotreating catalyst furtherly.

1. CATALYST SAMPLES

The residue hydrotreating unit of PetroChina under investigation in this work is one of the earliest fixed-bed residue hydrotreating units in China, and the processing capacity being 2.0 Mt/a. It is the key unit for processing imported high sulfur crude of the company. The feedstock is vacuum residue of Arabian light crude (ALVR) and the main product is high quality FCC feedstock.

The unit has two series of reactors and every series includes four single bed reactors. In fact, the reactor numbered 4 is the first reactor (guard reactor) in every series. In order to analyze and characterize the changes of chemical compositions and physical properties of catalysts along the catalyst bed, catalyst samples in different axial position of the catalyst bed were collected and analyzed at the end of an operation cycle.

The catalysts were sampled and reserved, and then extracted in a Soxhlet extractor to remove the adsorbed oil in laboratory. The pretreated catalysts were analyzed and the compositions and properties were determined. The basic information of the catalysts is given in Table 1.

Table 1
Basic Information of Catalyst Samples

Catalyst No.	Reactor No.	Catalyst species	Sampling location*
1	1	Ch-A	/
2	1	Ch-B	Top
3	1	Ch-B	Middle
4	1	Ch-B	Bottom
5	1	Ch-C	/
6	2	Ch-C	/
7	2	Ch-D	/
8	2	Ch-E	Top
9	2	Ch-E	Middle
10	2	Ch-E	Bottom
11	2	Ch-E	Bottom
12	3	Ch-F	Top
13	3	Ch-F	Bottom
14	4	Ch-G	/

*Sampling location refers to the sampling point in one grade catalyst bed.

Carbon, Hydrogen, Sulfur and Nitrogen contents on the catalyst samples were determined by Vario EL Ⅲ CNHS/O Elemental Analyzer. Metal elements were analyzed by wavelength dispersive X-ray fluorescence spectrometer (XRF).

2. ANALYSIS AND DISCUSSION

2.1 Element Composition of Fresh Catalysts

Catalysts were grading loaded in the fixed-bed residue hydrotreating unit. There are 11 kinds of catalysts from a famous catalyst company, having different functions in the unit. But there are only 5 kinds of catalysts playing leading roles in residue hydrotreating. The main element composition (not including Al_2O_3, which is the component of catalyst supporter) of fresh catalysts is given in Table 2.

Table 2
Elemental Contents of Fresh Catalysts

Catalyst pecies	w_{Mo} μg.g^{-1}	w_{V} μg.g^{-1}	w_{Ni} μg.g^{-1}	w_{Fe} μg.g^{-1}	w_{Co} μg.g^{-1}	w_{Ca} μg.g^{-1}	w_{Cu} μg.g^{-1}	w_{P} μg.g^{-1}
Ch-B	48530	0	3860	310	0	980	0	6690
Ch-C	59650	0	24630	140	60	2550	0	16510
Ch-E	85120	170	36380	170	0	900	0	17950
Ch-F	87310	340	29650	180	0	1030	80	18340
Ch-G	48790	0	8010	90	0	580	0	6610

The main active components of this catalyst series are Mo and Ni. The catalyst, with Mo-Ni as its active components has good hydrogenation activity and Mo-Ni is the most common combination style of hydrogenation component[1], which favors the reactions of HDN and HDM. Besides Mo and Ni, P exists widely in this catalyst series. P is one of the promoters of residue hydrotreating and can improve the hydrogenation performance of the catalysts, especially the performance of HDN and HDS[2].

As to other elements, such as Fe and Ca, their contents are low and they are not the necessary components of the catalyst. They may be mixed in during the course of production, storage and transportation.

2.2 Deposition Law of Nonmetal Elements on Spent Catalysts

At present, most of the researches about the deposition law of elements on spent hydrotreating catalyst were carried out with laboratory bench scale fixed-bed unit at different operation stages or different region in catalyst bed. It is a relative ideal reaction state because the control of operation conditions, flow states of gas and liquid, compositions of feedstock are different from which of commercial residue hydrotreating unit. Even though, no obvious law for the element deposition on catalyst along the bed was observed in most cases[3].

Nonmetal element contents on the spent commercial catalysts in this work are given in Table 3. Oxygen content is not discussed in this paper and the reason is as follows: (1) The catalyst itself contains massive oxygen because its supporter is Al_2O_3; (2) The coke on catalyst can be oxidized pre-and post the Soxhlet extraction in the course of storage and transportation. So the oxygen content cannot reflect the oxygen deposition on catalyst.

Table 3
Nonmetal Elemental Contents of Spent Catalysts

No.	Reactor No.	Catalyst species	w_H/%	w_C/%	w_N/%	w_S/%	w_{C+H}/%	n_H/n_C
1	1	Ch-A	1.04	11.19	0.23	12.87	12.23	1.11
2	1	Ch-B	0.89	10.40	0.21	19.20	11.29	1.02
3	1	Ch-B	1.39	19.42	0.35	7.89	20.81	0.85
4	1	Ch-B	1.04	10.05	0.20	21.46	11.09	1.23
5	1	Ch-C	1.44	22.38	0.34	5.88	23.82	0.77
6	2	Ch-C	1.29	15.21	0.30	8.30	16.50	1.01
7	2	Ch-D	1.42	17.23	0.33	6.31	18.65	0.98
8	2	Ch-E	1.36	15.88	0.32	7.65	17.24	1.02
9	2	Ch-E	1.33	14.68	0.31	8.79	16.01	1.08
10	2	Ch-E	1.32	15.03	0.31	9.11	16.35	1.05
11	2	Ch-E	1.32	15.99	0.32	7.22	17.31	0.98
12	3	Ch-F	1.44	19.5	0.32	5.92	20.94	0.88
13	3	Ch-F	1.13	11.62	0.23	12.78	12.75	1.16
14	4	Ch-G	1.24	20.27	0.34	14.75	21.51	0.73

It can be seen from Table 3 that the contents of C, H, S and N have not a change law along the catalyst bed. But there is an approximate inverse correlation between the contents of coke and sulfur on catalyst samples, that is, the catalysts with high sulfur contents have low coke contents.

The nitrogen contents are low and have comparatively great difference on different spent catalyst samples. It is found that the ratios between nitrogen to coke are in the range of 0.015~ 0.020. It shows that the nitrogen content in coke is relatively fixed and coke on catalyst should come from some substances which have fixed structure and composition in residue hydrotreating, which should be some condensed ring structures containing nitrogen and are difficult to hydrotreat in asphaltene. No similarity law was observed for the sulfur content because the sources and existing states of sulfur on catalyst are different. Besides reactive deposition, most of the sulfur comes from catalyst pre-sulfurization, so not all the sulfur on catalyst comes from the hydrotreating reaction and exists in coke.

H/C of coke on spent catalyst is also listed in Table 3. Most H/C of coke is above 0.8, and even a few above 1.2. Generally, H/C of coke on residue hydrotreating catalyst is much higher than that of FCC catalyst because of hydrogenation[1]. H/C of coke on spent catalyst is higher than H/C of hydrotreated asphaltene, even some original asphaltene[4]. The reasons are as follows: (1) Low H/C condensed ring structures in residue can be absorbed onto catalyst easily, and then deposited on catalyst by dehydro-condensation. (2) Most of the low H/C components on catalyst can hydrotreat and crack on the active hydrogenation centers because the catalyst has strong catalytic hydrogenation activity. Hydrogenation and cracking can make aromatic structure of asphaltene saturated, molecular weight decreased and adsorption capacity reduced. And then part of the deposited components can be desorbed from catalyst surface and enter the liquid when hydrogenation and cracking reaction goes to a certain extent. So, only the very low H/C components can be firmly absorbed on catalyst in residue hydrotreating. Most of the sediments on catalyst can be hydrotreated and desorbed and it isn’t genuine coke. Some researchers[3,5-9] advocated that coke on residue hydrotreating catalyst should be divided into different species. Commonly, coke on spent catalyst can be divided into low H/C and high H/C according to the element composition and conversion ability whatever type and name it is defined.

2.3 Deposition Law of Metal Elements on Spent Catalysts

Metal element contents on the spent catalysts in this work are given in Table 4. The main deposited metals on spent catalysts include V, Ni, Fe, Co, Cu, Ca, Sb in this commercial unit. Contents of other metals (such as Ti, Sr, Ru, Si etc.) are very low (only several to tens of μg.g^{-1}). This paper only discusses the deposition laws of main deposited metals.

Table 4
Metal Elemental Contents of Spent Catalysts

No.	Reactor No.	Catalyst species	w_V μg.g^{-1}	w_{Ni} μg.g^{-1}	w_{Fe} μg.g^{-1}	w_{Co} μg.g^{-1}	w_{Ca} μg.g^{-1}	w_{Cu} μg.g^{-1}	w_{Sb} μg.g^{-1}
1	1	Ch-A	82721	26832	2472	79	503	28	100
2	1	Ch-B	79883	26700	4393	98	530	23	101
3	1	Ch-B	26590	19322	4639	61	835	26	99
4	1	Ch-B	80058	26396	1844	80	330	24	77
5	1	Ch-C	7067	13436	8886	18	2804	25	92
6	2	Ch-C	20056	22979	3900	26	990	28	98
7	2	Ch-D	11590	16871	7314	25	1759	31	98
8	2	Ch-E	20017	20417	4132	28	947	20	91
9	2	Ch-E	29755	22975	2785	33	768	26	89
10	2	Ch-E	32360	22977	3889	35	990	25	87
11	2	Ch-E	18821	20117	1441	24	552	19	92
12	3	Ch-F	6440	14178	3277	12	1048	22	89
13	3	Ch-F	74072	25590	2286	72	417	25	94
14	4	Ch-G	27521	20499	2148	25	623	21	80

It can be seen from Table 4 that no necessary relation can be found for the contents of deposited metals on the spent catalysts along the bed. This is different from the results of Al-Dalama[10]. Al-Dalama found that the concentration of deposited vanadium decreased, while the content of carbon and the loss of surface area increased from the entrance to the exit in a commercial fixed-bed unit. But the catalyst samples used by Al-Dalama are lack of representation because only four samples were analyzed for the entire reactor series (only one sample for each reactor) and no information about the sampling position in the reactors was given. Xu X. K. *et al.*[11] found that the amount and composition of deposited elements on spent catalyst are random not only along the bed height, but also with the position in the same height in the guarded fixed-bed reactor.

Through comparison between Table 3 and Table 4, it can be seen that besides the Mo and Ni which are contained in fresh catalysts, other metal elements such as V, Fe, Co, Cu, Ca and Sb can be observed on the spent catalysts. V, Ni, Fe and Co etc. come from the hydrogenolysis and deposition of organometallic compounds in the feedstock. The increase of V is much greater than that of Ni on the spent catalysts because the content of V in the feedstock is higher than Ni[12].

Because the contents of C and H on catalyst can't be analyzed by XRF, the metal contents in Table 4 have been obtained by direct XRF analysis of the coked catalyst and then normalized according the analysis results from CNHS/O Elemental Analyzer. In order to detect and correct the influence of coke on analysis results of metals, the burned catalyst (burning conditions are 450 ℃ and in the air atmosphere for 4 h) were analyzed by XRF. Analysis results for main metals on the burned catalysts are given in Table 5.

Table 5
V and Ni Contents of Burned Spent Catalysts

No.	Reactor No.	Catalyst species	V, wt%	Ni, wt %
1	1	Ch-A	12.376	4.963
2	1	Ch-B	14.769	6.095
3	1	Ch-B	6.209	4.831
4	1	Ch-B	15.018	5.965
5	1	Ch-C	1.522	4.138
6	2	Ch-C	3.828	5.653
7	2	Ch-D	2.136	4.450
8	2	Ch-E	3.619	5.110
9	2	Ch-E	5.624	5.637
10	2	Ch-E	5.894	5.581
11	2	Ch-E	3.540	4.903
12	3	Ch-F	1.200	3.927
13	3	Ch-F	13.312	5.630
14	4	Ch-G	11.620	5.410

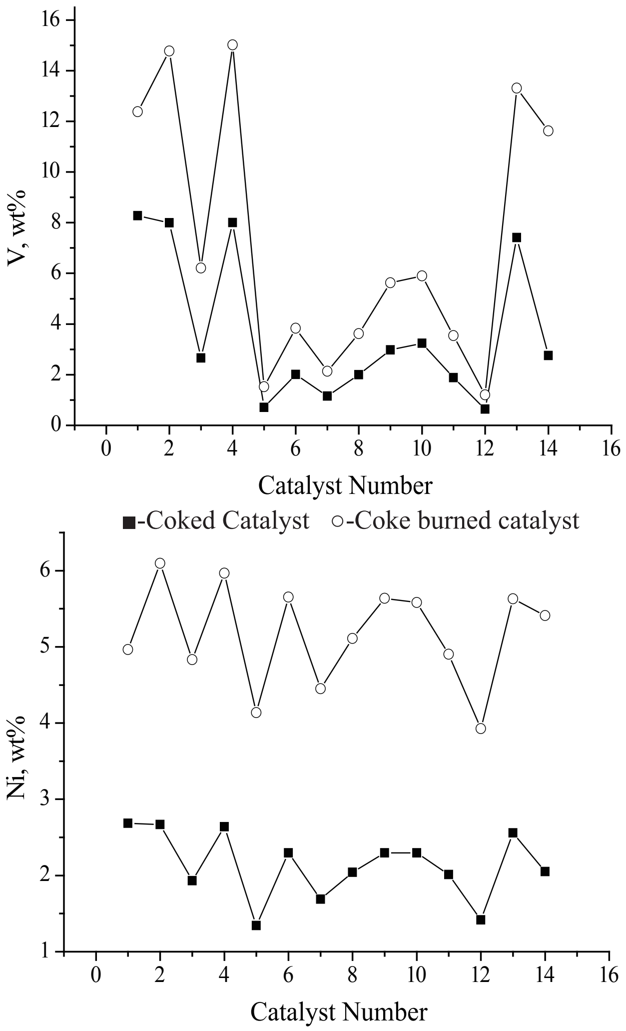

Figure 1
Content Changes of V and Ni Along Catalyst Bed

Similarly, no necessary relation was found for the contents of deposited metals on the burned spent catalysts along the bed. The distributions of V and Ni on spent catalysts are consistent with that of the burnt spent catalysts, although the metal contents pre- and post burning are different because of the changes of C, H, S and N on catalyst caused by burning (see Figure 1). The above conclusions are further verified by Figure 1, that there are no necessary relations for metal contents on spent catalysts along the catalyst bed at the end of one operation cycle.

2.4 Internal Relations of Deposited Elements on Spent Catalysts

The content of coke and metals deposited on the commercial catalysts is scattered along the catalyst bed which is different from the results in literatures, especially the results from laboratory residue hydrotreating units. The metals content on catalyst still changed irregularly even if the metal contents on different grades fresh catalyst are put into consideration. Whether or not the catalyst samples or analysis methods exist any problems?

The catalyst samples were collected when catalyst-unloading was carried out to a certain stage and the catalysts unloaded from a certain location were well-mixed before sampling. So the catalyst samples should have a good representativeness. The scattered sediments data along the catalyst bed is mainly related to the local flowing state, mass transfer performance, and reaction conditions in the fixed-bed reactor, such as the uniformity of catalyst loading, the occurring of wall-flow, channeling, hot and cold spots etc. Xu X. K. *et al.*[11] analyzed the sediment composition on a kind of commercial residue hydrotreating catalysts at different height or different azimuth at the same height of catalyst bed from a prepositive reactor. Their results also confirmed that contents of coke and metals on spent catalysts were scattered (even for different azimuth at the same height). Fixed-bed residue hydrotreating is a gas-liquid-solid three-phase reaction, and the flow state is lying between trickle flow region and pulse flow region. The reactant distribution along the radius of catalyst bed appears inhomogeneous because of channeling or bias flow which was caused by the initial maldistribution of liquid phase in catalyst bed, the size distribution of catalyst particles, uniformity of catalyst filling and voidage distribution of catalyst bed, etc.. The reasons presented above can cause uneven distribution of hydrogenation and emergence of hotspot or coldspot in reactor because residue hydrotreating is a strongly exothermic reaction. And then, the temperature asymmetry can result in great asymmetry of chemical reaction rate at different reactor positions. So the uniformity of the chemical reaction was broken and side-reactions increased locally which lead to the deposition of metals and coke change irregularly. A piece of coked catalyst (about 30cm across) has been taken out from residue hydrotreating reactor which was possibly come from material and temperature inhomogeneous distribution in reactor[12].

In order to verify the accuracy of analysis method in this work, parallel experiments were performed. The analysis results are just the same for different batches of the same catalyst sample. And then, some meaningful results were obtained by thorough studying of the analysis results for the spent catalysts.

Firstly, the catalysts with high metal contents also have high sulfur contents which can be obtained by comparing the data in Table 3 with Table 4. According to relevant research[13-15], metals (such as Ni, V, Fe, Ca, and so on) removed from residue were deposited on catalyst in forms of metal sulfides during the residue hydrotreating. So the sulfur content on catalyst increased with increasing of metal content. But the content of sulfur is disproportionate to that of metal on spent catalyst because parts of sulfur exist in forms of organic sulfide in coke rather than metal sulfides. The analysis results of element contents are well coincide with the results of theoretical analysis.

Secondly, it can be seen from the data in Table 3 and 4 that the catalysts with high metal contents have low contents of coke and high H/C. Residue hydrotreating is a metal catalyzed reaction and the active hydrogenating components are metal sulfides of Mo, Ni and Co, etc.. Hydrogenation activity of catalyst should gradually decrease because the coke deposition on the catalysts and cover the active centers. Theoretically, catalyst should totally inactivate because massive coke can completely cover the active centers of the catalyst when the reaction goes to a certain degree.

In fact, the catalyst still retained some activity when deposition amount of coke reached to about 25% (see table 3) in operation process. This is because that the hydrogenation activity of catalyst does not comes from the supported active metal components totally, part of it arise from the deposited metal sulfides (especially sulfide of Ni). Jia Y. Z.[16] has discussed autocatalysis of deposited Ni and V on catalyst theoretically in residue hydrotreating, but did not confirm it in industrial process. The deposited metal sulfides of Ni and V mixed with coke which was exposed on catalyst surface were the main hydrogenation active components in the middle-later operating cycle of fixed-bed residue hydrotreating. The metal sulfides can depress condensation reaction significantly, and the condensation products (especially the condensation products around deposited metal sulfides) on catalyst were hydrogenated and even desorbed from catalyst. So the catalysts with high deposited metals have low contents of coke and high H/C. These results in this work confirmed that commercial fixed-bed residue hydrotreating is an autocatalytic process. The removed metals deposited on catalysts in forms of metal sulfides can act as an important role in residue hydrotreating .

CONCLUSIONS

The contents of various deposited elements on spent catalysts showed scatter data along the bed in commercial fixed-bed residue hydrotreating unit. The deposition amounts of elements on spent catalyst mainly depend on local reaction conditions and catalyst loading state in fixed-bed.

Catalysts with high metal depositions have low contents of coke, high contents of sulfur and H/C, which shows that deposited metals were in forms of activated metal sulfides. Commercial residue hydrotreating is an autocatalytic process.

The ratios of nitrogen to coke on catalysts are almost all between 0.015 and 0.020. The coke on residue hydrotreating catalysts comes from some specific condensed ring structures containing nitrogen which is difficult to hydrotreat in asphaltene.

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