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Properties Analysis of Spent Commercial Residue Hydrotreating Catalyst: Surface Property Changes of Spent Catalysts in Commercial Residue Hydrotreating Unit

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In this study, the changes of the surface properties of 14 spent catalysts, which were sampled from a commercial residue hydrotreating unit at the end of an operation cycle, were analyzed and compared with the corresponding fresh catalysts. It was found that the changes in the surface properties do not have change laws along the bed height. Furthermore, the pore size, pore volume and surface area of most of the catalysts decreased after reaction and the number of micropores of the spent catalysts increased, due to the fact that the coke and metals deposited in the catalyst to alter the pore distribution. But some catalysts with high coke content, the pore size and pore volume decreased with the increase of surface area, which was a result of the forming of massive micro/mesopores (the pore size is mainly ranged from 3 to 10 nm), when partial soft coke desorbed under the action of the deposited active metals and micro/mesopores were formed in macropores or large mesopores. The surface properties of the spent catalysts were not only related to the deposition amounts, but also to the deposition configurations of the coke and metals on the catalysts.

Key words: Spent catalyst; Residue hydrotreating; Surface property; Changes

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INTRODUCTION

Residue hydrotreating catalysts are manufactured by immobillized active metals on porous acidic supports, such as alumina, zeolite, activated carbon and some metal oxides, etc. The common characteristic among all supports is that they are porous solid materials with high surface areas. The active metals should have higher and more accessible surface areas when being supported on the internal and external surfaces of the supports. High surface area is one of the necessary properties of residue hydrotreating catalysts, and is also capable of reducing the consumption of expensive metals and the production costs of the catalysts.

In residue hydrotreating, with an increase in reaction time, the carbon residue, asphaltene and metal in the residue were continuously deposited on the catalysts in the forms of coke and metal sulfides. The deposited coke and metal sulfides can cover active points, reduce or block micropores, increase steric effects and diffusion resistance, and impede the reactants from entering the catalyst pores and contacting the internal catalyst surface (Van Dongen, Bobe, Van der Eijk, & Van Klinken, 1980; Galiasso, Blanco, Gonzalea, & Quinteros, 1983; Ancheyta, Betancourt, Centeno, & Marroquín, 2003; Jiang, Weng, & Liu, 2010; Tailleur & Caprioli, 2005). Therefore it may be seen that as a result of catalyst activity decreasing, the conversion and reaction rates of residue hydrotreating were greatly reduced. Due to the graded loading patterns of the catalysts, the types and amounts of coke and metal sulfides differed among different sites of the reactors for the various catalysts and main reactions (Al-Dalama & Stanislus, 2006; Sun & Wang, 2005). It is helpful to understand the causes of the deactivation of residue hydrotreating catalysts by systematically studying the configuration deactivation of the catalysts in different commercial reactor sites, and also has important guiding and practical significance for catalyst development, especially for the optimal design of pore structure of the support for residue hydrotreating catalysts.

1. CATALYST SAMPLES

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

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	/

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

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

In the laboratory, the catalysts were sampled and reserved, then extracted using a Soxhlet extractor to remove the adsorptive oil. The pretreated catalysts were analyzed and their respective compositions and properties were determined. The basic information of the catalysts is shown in Table 1.

2. SURFACE PROPERTY ANALYSIS OF CATALYSTS

The surface area, pore volume and pore size of the catalysts were analyzed using an ASAP 2020M surface area and porosity analyzer, manufactured by Micromeritics. The ASAP 2020M is capable of measuring the surface area of catalysts and analyzing pore size distribution in the range of 3.5 to 5000 Angstrom.

The analysis results of the surface properties of 14 spent catalysts and the corresponding fresh catalysts are shown in Table 2.

Table 2
Analysis Results of Catalyst Surface Properties

Catalyst species or No.	BET surface aream^2/g	Micropore surface area m^2/g	Pore volume cm^3/g	Average pore diameternm
1	114.02	19.36	0.1598	5.61
Ch-B fresh	105.01	9.49	0.5590	20.08
2	102.33	25.68	0.1375	5.21
3	448.92	/	0.6647	5.96
4	99.37	16.27	0.1465	5.48
Ch-C fresh	99.28	8.69	0.5779	21.85
5	96.97	23.54	0.1586	6.52
6	128.03	31.37	0.2141	6.73
7	135.32	20.63	0.2197	6.49
Ch-E fresh	149.36	10.84	0.5420	14.10
8	122.64	27.56	0.2226	7.19
9	132.12	26.01	0.2316	6.90
10	91.84	11.46	0.1825	7.60
11	123.25	30.81	0.2235	7.22
Ch-F fresh	183.1	13.95	0.5057	10.72
12	117.62	22.48	0.1967	6.59
13	126.76	35.02	0.1504	4.73
Ch-G fresh	130.95	15.25	0.6733	19.33
14	537.39	/	0.6328	4.75

3. ANALYSIS AND DISCUSSION

When the residue hydrotreating reactions have been performed, the continuous deposition of coke and metals on the internal and external surfaces of the catalysts led to changes in the pore structure of the catalysts. The pore size, pore volume and surface area of the catalysts continuously decreased during residue hydrotreating. It can be seen from Table 2 that the average pore sizes of all the spent catalysts significantly decreased, as did the surface area and pore volume, with the exceptions of catalysts 3, 6 and 14.

The feedstock included massive components of high molecular weight and large diameter (such as asphaltene) in residue hydrotreating. The support of residue hydrotreating catalysts usually adopts mesoporous materials in order to reduce the diffusion resistance of macromolecules. The pore size of support commonly ranges from several to tens of nanometers. This type of pore size distribution not only ensured that the catalysts would possess large surface areas, but also that the diffusion resistance in the catalyst pores would be reduced. Therefore it is beneficial to promote residue hydrotreating reactions. With an increase in reaction time, the coke and metals deposited on the walls of the catalyst pores led to changes in pore size distribution. The respective pore size distributions of some fresh and spent catalysts are shown in Figures 1 and 2. The pore size distribution of the fresh catalysts was more uniform than that of the spent catalysts, mainly ranging between 10 and 40nm. While the pore size distributions of the spent catalysts had clearly been broadened, the number of micropores increased remarkably. These micropores originated from the meso/macro-pores, of which the pore sizes were decreased by coke and metal deposition.

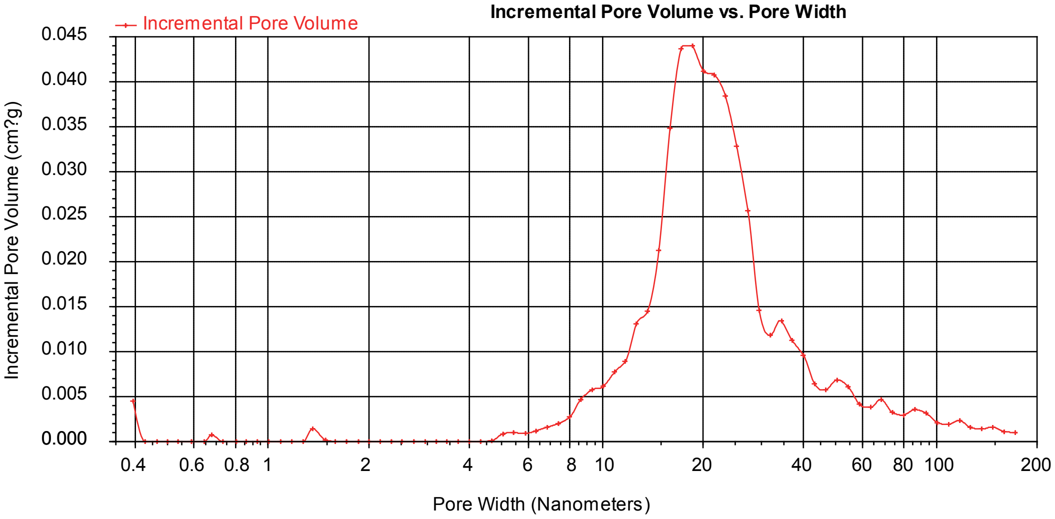

Figure 1
Pore Size Distribution of Ch-B Fresh Catalyst

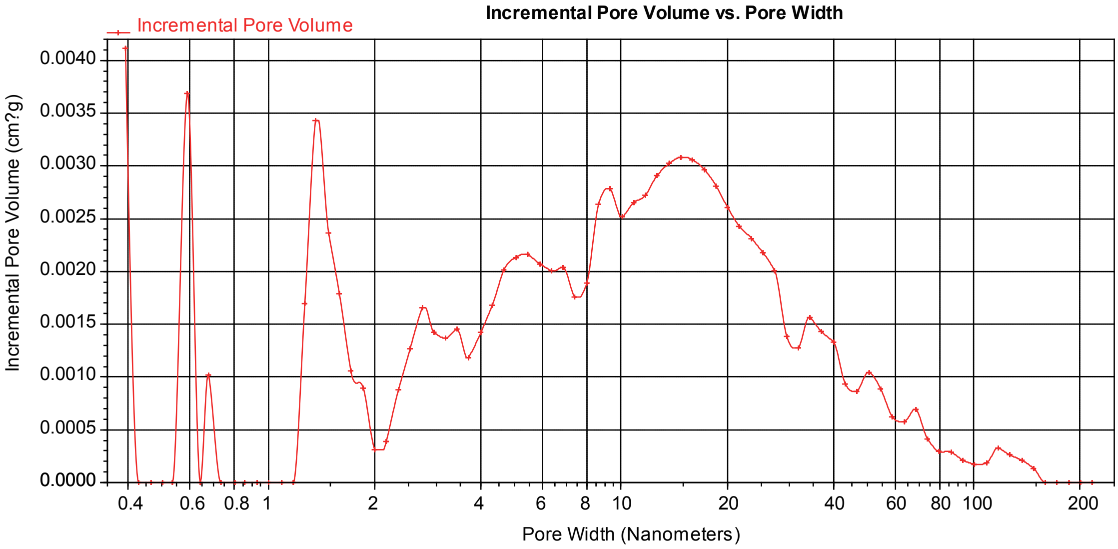

Figure 2
Pore Size Distribution of Spent Catalyst 2

Zhang, Ma, Li, Liu, Geng, & Wang (2008) pointed out that coke deposition was the main cause of catalyst deactivation. Coke deposition can create clear alterations to the surface properties of catalysts. It may be seen from the data shown in Table 2 that the decrease in surface area and pore volume differ even for the same type of catalyst. Furthermore, there is no fixed relationship between the deposition amount of coke and the loss of surface area or pore volume. For example, the coke contents of catalysts 9 and 11 were similar to or even slightly higher than that of catalyst 10, these are all the same type of catalyst, but the pore volume and surface area of catalyst 10 are far lower than those of the other two. These results indicate that the surface properties of spent catalysts are not only related to the amount of sediments, but are also closely related to the deposition configurations of the sediments.

One possible situation is that coke and metals rapidly deposit on and block the entrance of catalysts at the beginning of the reaction, thus causing great loss of pore volume and surface area, although the deposition amounts of coke and metal are comparatively low. A second possibility is that the coke and metals are not homogeneously deposited on the pore walls of the catalyst by layer, and the deposition configurations of the coke and metals are related to the surface characteristics of the catalyst, especially to the distribution of the metal active components on fresh catalysts. The reason for the uneven distribution of coke and metals on spent catalysts in residue hydrotreating is that heavy metals in residue are inclined to remove and deposit on sites of high active metal content, while coke is inclined to deposit on sites of low active metal content. The deposited metals on catalyst also have hydrogenation activity in residue hydrotreating. Once this uneven distribution occurs, it should continue to the end of an operation cycle. The changes in catalyst surface properties differed from one another because the coke and metal deposition in catalyst pores were uneven.

For most of the spent catalysts, the deposition of coke and metals led to a decrease in pore size (or even a blockage of pores), pore volume and surface area. The surface areas of some catalysts may increase while their pore sizes and volumes decrease, due to the fact that coke and metals deposit unevenly in catalyst pores, causing roughness in the inner wall. Compared with the corresponding fresh catalysts, the surface areas of spent catalysts 3, 6 and 14 increased, instead of decreased. The surface areas of catalysts 3 and 14 were approximately four times those of the corresponding fresh catalysts. These results differ from the traditional understanding of the surface property changes of spent catalysts in residue hydrotreating.

Through analysis of the surface property results, it may be seen that the pore structures of catalysts 3 and 14 are remarkably different from those of the other spent catalysts. The pore size distribution of catalyst 3 is shown in Figures 3, where it may be seen that it is similar to those of catalysts 6 and 14. It can be seen from figure 3 and figure 4 that the pore size has been decreased greatly and a great part of the pores were distributed in the range of microporous.

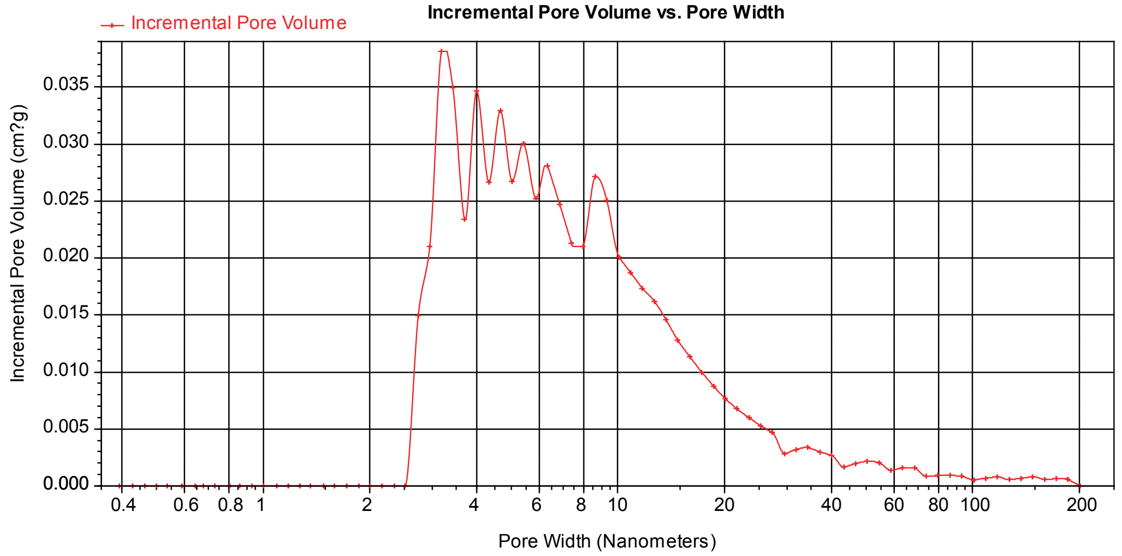

Figure 3
Pore Size Distribution of Spent Catalyst 3

In general, coke and metals were deposited on the pore walls, then grew layer by layer along the pore walls from the outside to the inside (see Figure 5(b)). With the deposition of coke and metals, the pore sizes, pore volumes and surface areas decreased continuously. But in some special cases, coke and metals were not deposited on the catalyst pore walls layer by layer, but to form some new structures via forming micropore in macropores or large meso-pores. Thus massive micropores or small meso-pores were formed in the new structure via pore-making (see Figure 5(c)). In this case, although the average pore size and pore volume decreased, the surface area increased because massive new pore walls were formed via pore-making. This is the main factor which caused the surface areas of spent catalysts 3, 6 and 14 to increase.

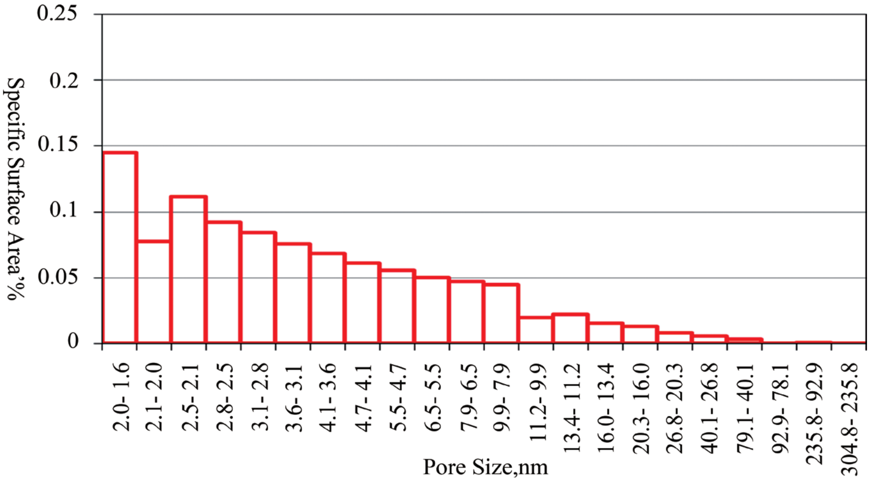

Figure 4
Distribution Map for BJH Specific Surface Area & Pore Size of Spent Catalyst 3

Figure 5
Different Pore Structures of Catalyst
(a) Pore of Fresh Catalyst (b) Pore of Normal Deposition (c) Pore-Making in Catalyst Pore

As the catalysts of surface area increased, the carbon contents of catalysts 3 and 14 increased by approximately 20% (Sun, Yang, & Liu, 2012), and the surface areas of catalysts 3 and 14 also increased significantly. Under the proper reaction conditions, the deposited coke was able to form sediment similar to activated carbon in residue hydrotreating. The activated carbon has large surface areas, with some reaching as high as $2000m^2/g$. Therefore, rather than decreasing, the surface area of some spent catalysts with high coke content increased instead. This type of phenomenon is more likely to appear in the case of coke and metals being co-deposited on the catalysts. Partial soft coke around deposited metals which possessed hydrotreating activity were able to hydrotreat and be desorbed from the catalyst, so that massive micro/mesoporous structures were generated at the position of the desorbed soft coke, and the surface area of the catalysts increased significantly. It is indirectly proved that the residue hydrotreating is an autocatalytic reaction.

CONCLUSIONS

① Along the fixed-bed height, the surface property changes of spent catalysts possessed no change laws in commercial residue hydrotreating reactors.

② The pore size, pore volume and surface area of most catalysts decreased after reaction, due to the coke and metal sulfides which were deposited on the internal and external surfaces of the catalysts.

③ Rather than decreasing, the surface area of some catalysts with high coke content increased instead. Surface area increase was caused by the formation of massive micro/mesopores when partial soft coke desorbed under the action of deposited active metals, and new structures were formed in macropores or large meso-pores.

④ The surface area changes of the spent catalysts were not only related to deposition amounts, but also to the deposition configurations of the coke and metals on the catalysts.

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