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Preparation of heavy oil hydrotreating catalyst from spent residue hydroprocessing catalysts

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Abstract

In recent years, increasing emphasis has been placed on recycling spent hydroprocessing catalysts due to environmental regulations which list them as hazardous waste materials. In the present work, the recycling of spent residue hydroprocessing catalysts that contained high levels of vanadium was investigated by using them in the preparation of active new hydrotreating catalyst after subjecting them to different treatments such as decoking, acid-leaching and hydrothermal treatment. Catalyst extrudates containing different levels of V, Mo and Ni on Al_2O_3 were prepared by mixing the spent catalyst powder with boehmite in different proportions followed by peptization, kneading and extrusion. The prepared catalyst extrudates were characterized by chemical analysis and surface area and porosity measurements. The HDS and HDM activities of the catalysts were tested using Kuwait atmospheric residue as feed and compared with that of a reference HDM catalyst. Partial leaching of vanadium from the spent catalyst opened up the pores, and the catalyst prepared by mixing the metal-leached spent catalyst (MLSC) with boehmite had higher surface area and pore volume and showed higher hydrotreating activity than that prepared from unleached spent catalyst. Hydrothermal treatment of the spent catalyst increased its porosity and surface area. Catalysts prepared from hydrothermally treated spent catalyst (HTSC) had higher surface area and pore volume and showed higher HDM and HDS activities than that prepared from the spent catalyst without hydrothermal treatment. The catalysts prepared from the treated spent catalysts also exhibited substantially higher HDM and HDS activities than the reference commercial HDM catalyst. The results indicate that spent catalysts containing high levels of vanadium together with Mo and Ni on Al_2O_3 can be used in the preparation of active HDM/HDS catalysts, and thereby, their environmental problem can be reduced.

Keywords: Spent catalyst recycling; Waste utilization; Residue hydrotreating; HDM catalyst

1. Introduction

Solid catalysts are widely used in many processes in the petroleum refining industry [1]. Catalysts facilitate difficult hydrocarbon transformations with high selectivity and permit the refiners to produce the full range of clean transportation fuels with desired specifications from petroleum distillates and residues [2]. Thus, for example, catalytic processes such as naphtha catalytic reforming, isomerization, alkylation and catalytic cracking are responsible for the production of high octane gasoline [2,3]. Production of clean diesel fuels with low-sulfur levels is achieved by hydrotreating of sulfur-containing gas oil streams in the presence of catalysts [4–7]. Catalysts are also extensively used in the conversion of heavy oils and residues to more valuable light and middle distillates [8–10].

Among the various processes in the petroleum refining industry, catalytic hydrotreating processes consume large quantities of catalysts for the purification and upgrading of various petroleum streams and residues [11]. In the residue hydrotreating process, the catalysts, which consist of Mo with promoters such as Co or Ni on alumina support, promote the removal of undesirable impurities such as sulfur, nitrogen and metals in the feed by hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetallization (HDM) reactions [12–15]. However, the catalysts used in this process deactivate rapidly by coke and metal (V and Ni) deposition, and have a short life [16,17]. Since the technology for regeneration and reactivation of the catalysts deactivated by metal fouling is not available to the refiners, the spent catalysts are discarded as solid wastes [18–20].

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The amount of spent hydroprocessing catalysts discarded as solid wastes has increased significantly in recent years because of a steady increase in the processing of heavier feedstocks containing higher sulfur, nitrogen and metal (V and Ni) contents, and due to a rapid growth in diesel hydrotreating capacity to meet the increasing demand for low-sulfur fuels. At the same time, environmental laws concerning spent catalyst disposal have become increasingly more severe in recent years. Spent hydroprocessing catalysts have been classified as hazardous wastes by the Environmental Protection Agency in the USA [21,22]. Several alternative methods such as disposal in landfills, reclamation of metals, regeneration/rejuvenation and reuse, and utilization as raw materials to produce other useful products are available to the refiners to deal with the spent catalyst problems [20,23–25]. As the disposal of spent catalysts as landfill is environmentally restricted, increasing emphasis has been placed on the development of processes for recycling the waste catalyst materials as much as possible. Recovery of metals and other components from the spent catalysts is possible, particularly for the catalysts which contain valuable metals in high concentrations, and research in this area is continuing worldwide [26,27].

Utilization of spent catalysts as raw materials in the production of other valuable products is an attractive option for their recycling from environmental and economical points of view. Spent fluid catalytic cracking (FCC) catalysts have been successfully used in cement production [25,28]. Recently, a process for making highly stabilized non-leachable synthetic aggregates and ceramic materials from spent catalysts has been reported by Sun et al. [29]. A few studies on the preparation of active catalysts from spent catalysts for various applications have been reported in the literature. Lee et al. [30] reported that active reforming catalysts can be prepared using the V, Ni and Mo containing extract obtained by leaching spent catalysts with citric acid. Furimsky [31] found that spent Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts, after regeneration, could catalyze the decomposition of H_2S. In a recent patented process, Choi et al. [32] used spent hydroprocessing catalysts to prepare active catalysts for reduction of nitrogen oxides. The use of spent catalysts in the preparation of active hydrotreating catalysts have been reported in a few earlier studies [33,34]. However, the spent catalysts used in these earlier works were from petroleum distillate hydrotreating units and contained Mo, Co and Al_2O_3 without V.

Spent catalysts containing high levels of vanadium, together with Mo and Ni are discarded as solid wastes in large quantities in Kuwait refineries. Over 250,000 barrels of residues are upgraded and converted to high quality products by catalytic hydroprocessing in the three refineries of Kuwait bringing substantial economic returns to the country. These operations, however, generate a large amount of spent catalysts as solid wastes every year. Currently, about 6000 t of spent hydroprocessing catalysts are discarded as solid wastes from the three refineries in Kuwait. This will increase further and exceed 10,000 t/year when a forth refinery is built to process heavy crudes and residues. Therefore, handling and utilization of spent residue hydroprocessing catalysts was considered as an important area for research in our laboratory. In most of our previous studies, rejuvenation and reactivation of spent residue hydroprocessing catalysts that were deactivated by coke and metal (V + Ni) deposits was addressed [35–40]. In continuation of our research on recycling and utilization of spent catalysts, recently, we focused our attention on the preparation of active hydrodemetallization catalysts from spent residue hydroprocessing catalysts that contained V, Mo, Ni and Al_2O_3 together with coke, by mixing and extruding them with boehmite.

In a previous paper [41], we compared the physical and chemical properties and the HDM and HDS activities of catalysts prepared from three types of spent catalyst that contained different levels of vanadium. The catalyst prepared from the high-vanadium containing spent catalyst showed relatively low HDM and HDS activity due to its low surface area, pore volume and high vanadium content. In the present work, we have investigated the utilization of spent residue hydroprocessing catalysts that contained high levels of vanadium in the preparation of active new hydrotreating catalysts after subjecting them to different treatments such as acid-leaching and hydrothermal treatment to reduce the fouling effect of vanadium. Catalysts prepared from the treated catalysts had higher surface area and pore volume and exhibited higher HDM and HDS activity than that prepared from the untreated spent catalyst.

2. Experimental

2.1. Pretreatment of spent catalyst

Spent catalyst was obtained from Kuwait National Petroleum Company (KNPC). The spent catalyst was first washed with naphtha and then extracted with toluene in a soxhlet apparatus to remove the residual oil. It was then decoked by combustion of coke under programmed and controlled temperature conditions in the range 300–500 °C in an oxygen atmosphere (i.e. 5% O_2 in N_2). The decoked spent catalyst contained 11.1 wt% V, 4.9 wt% Ni and 5.4 wt% Mo on Al_2O_3. It was then subjected to metal-leaching and hydrothermal treatments. Oxalic acid (5%) was used for partial leaching of the metals from the spent catalyst. Hydrothermal treatment was conducted in an autoclave at 300 °C for 2 h. The treated and untreated (decoked) spent catalysts were crushed and ground to fine powder (particle size 25–90 μm) before using them in catalyst preparation experiments.

2.2. Preparation of catalyst extrudates

Catalyst extrudates containing different levels of V, Mo and Ni on Al_2O_3 were prepared by mixing the spent catalyst with boehmite in different proportions followed by peptization, kneading and extrusion. Boehmite used in the catalyst preparation experiments were obtained from Sasol, Germany. The sequence of operational steps used for the preparation of catalyst extrudates from spent catalyst/boehmite mix in the present work are shown in Fig. 1.

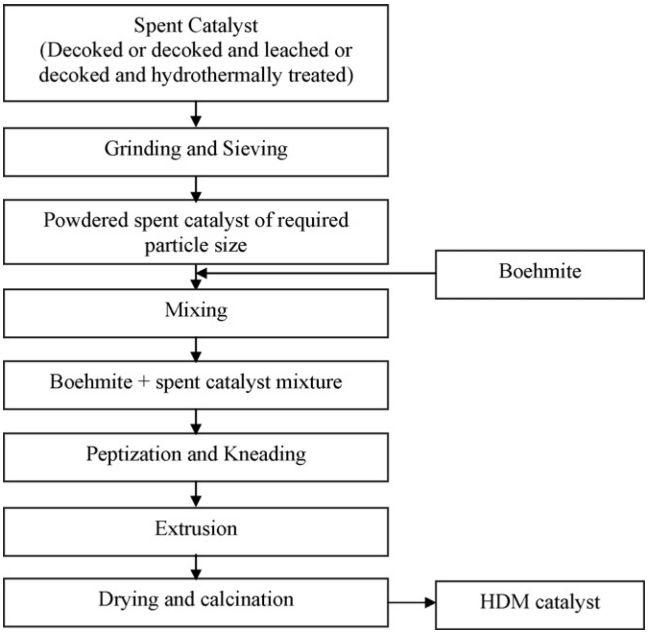

Fig. 1. Operational steps in the preparation of catalyst extrudates from spent catalyst.

A laboratory kneading and extrusion machine (Type: LUK. 2.5 AS) manufactured by Werner and Pfleiderer & Co., Germany, was used for the preparation of catalyst extrudates from spent catalyst/boehmite mixtures. It contained a mixing chamber, two blades for mixing, and a drive unit with two three-phase motors and gears, and a discharge screw.

Three hundred grams of spent catalyst/boehmite mixture in the desired mixing ratio was taken in the mixing chamber for each experiment. Then 185 ml of dilute nitric acid (e.g. 2%), as a peptizing reagent, was added in drops at a constant rate to the boehmite/spent catalyst mix and kneaded. The blades in the mixing chamber were counter rotating and turned at different speeds. They were designed and arranged for intensive mixing and kneading of the material with the nitric acid to form a good, extrudable paste.

At the end of the mixing and kneading time (20–30 min), the product was extruded by means of the discharge screw through a die containing several holes (1.5 mm in diameter) to form catalyst extrudates. The extrudates were dried at 110 °C in an oven for 24 h and calcined at 450–500 °C. After calcinations the prepared extrudates were cooled in desiccators and characterized.

2.3. Catalyst characterization

The concentrations of V, Mo and Ni in the spent catalyst and in the prepared catalyst samples were determined by inductively coupled plasma atomic emission spectroscopy (Varian Liberty II ICP-AES). Surface areas of the catalysts were determined by BET method using an autosorb adsorption unit manufactured by Quantachrome Corporation, USA. A mercury porosimeter (Quantachrome Poremaster – 60) was used for pore volume and pore size distribution determination in catalyst samples.

2.4. Catalysts activity testing

Hydrotreating activities of the prepared catalysts were tested in a high pressure fixed bed microreactor unit using Kuwait atmospheric residue as feed. The feedstock contained 4.3 wt% sulfur, 0.27 wt% nitrogen, 69 ppm vanadium, 21 ppm nickel, 3.6 wt% asphaltenes and 12.4 wt% CCR. Thirty milliliters of the catalyst diluted with an equal amount of carborundum was used for each run. The catalysts were presulfided before introducing the feed using 3 wt% dimethyl disulfide (DMDS) in straight run gas oil by a standard procedure [15]. After presulfiding, the test conditions were adjusted to desired operating temperature, pressure, hydrogen to oil ratio and liquid hourly space velocity (LHSV). All catalysts were tested under the following operating conditions:

$$\text{pressure} = 120\,\text{bar};\quad \text{LHSV} = 1\,\text{h}^{-1};\quad \text{H}_2/\text{Oil ratio} = 1000\,\text{ml}/\text{ml};\quad \text{temperature} = 370\,^{\circ}\text{C}$$

A commercial HDM catalyst (MoO_3/Al_2O_3; 4 wt% Mo; surface area, 170 m^2/g; pore volume, 0.6 cm^3/g) catalyst was also tested under the same operational conditions. For each run, product samples were collected every 24 h for analysis of S and V content. Sulfur content was determined using an Oxford Model 3000 XRF instrument. The concentration V in the feed and product oil samples was determined without ashing using a Varian Liberty Series II, ICP spectrophotometer.

3. Results

3.1. Characteristics and HDM/HDS activities of the catalyst prepared from leached spent catalyst

The spent catalyst (decoked) was treated with 5% oxalic acid solution to partially leach the deposited metals. Surface area, pore volume and metals content of the spent catalyst before and after the metal-leaching treatment are compared in Table 1. It is seen that the spent catalyst contains 11.1wt% V, 5.4wt% Mo and 4.9 wt% Ni, and has very low surface area and pore volume. About 35% of V, 30% of Mo and 45% of nickel have been removed from the catalyst by leaching. Substantial improvement in the surface area and pore volume of the catalyst has occurred as a result of extraction of the metals. Leaching of the foulant metal deposits blocking the catalyst's pores could open the pores and consequently increase the pore volume and surface area of the catalyst.

Table 1
Spent catalyst properties before and after metal-leaching treatment

Properties	Spent catalyst (before leaching)	Spent catalyst (after leaching)
Surface area (m^2/g)	37	86
Pore volume (cm^3/g)	0.24	0.34
Vanadium (wt%)	11.1	7.3
Molybdenum (wt%)	5.4	3.8
Nickel (wt%)	4.9	2.7

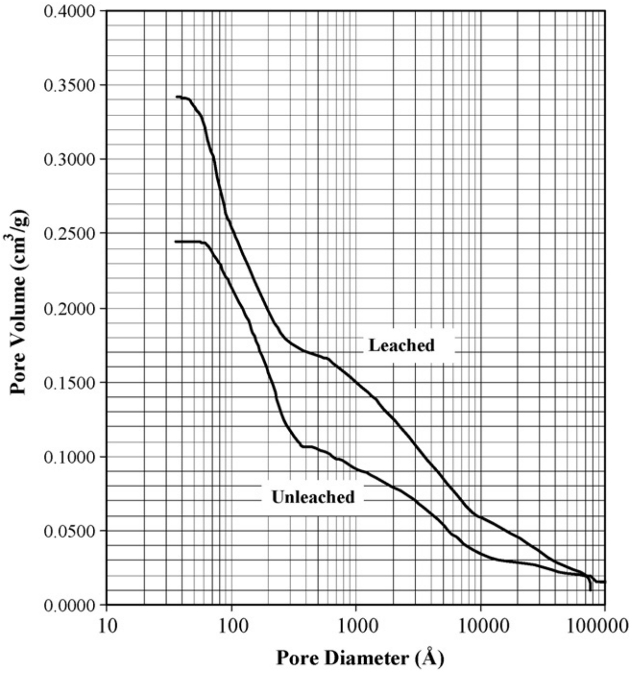

Fig. 2. Comparison of pore size distribution of leached and unleached spent catalysts.

The pore size distribution data for the spent catalyst before and after metal leaching are compared in Fig. 2. The volumes of both the narrow pores (50–300 Å) and the large pores in the range 1000–8000 Å have increased by leaching a portion of the metals from the spent catalyst.

Catalyst extrudates were then prepared from the MLSC by mixing, kneading and extrusion with boehmite in accordance with the standard procedure described in Section 2. Three catalysts were prepared by mixing leached spent catalyst with boehmite in different percentages (i.e. 20%, 40% and 60%). The prepared catalysts were characterized and their HDS and HDM activities were tested in a microreactor. In Figs. 3 and 4, the effects of adding increasing amounts of MLSC to boehmite on the surface area and pore volume of the prepared catalysts are shown. The surface area and pore volume data for the catalysts prepared from the unleached spent catalyst by the same procedure are also included in these figures for comparison.

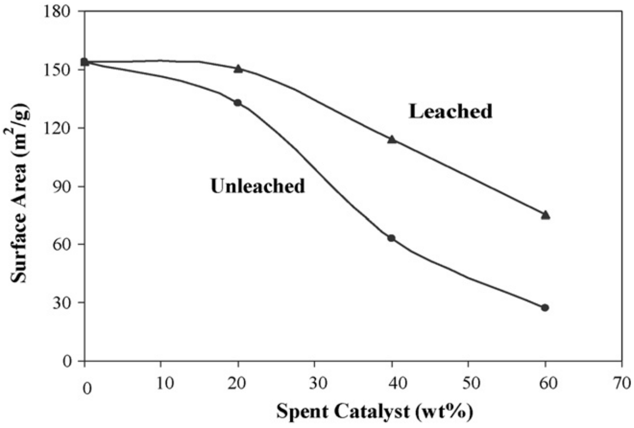

Fig. 3. Surface area comparison between the catalysts prepared from leached and unleached spent catalysts.

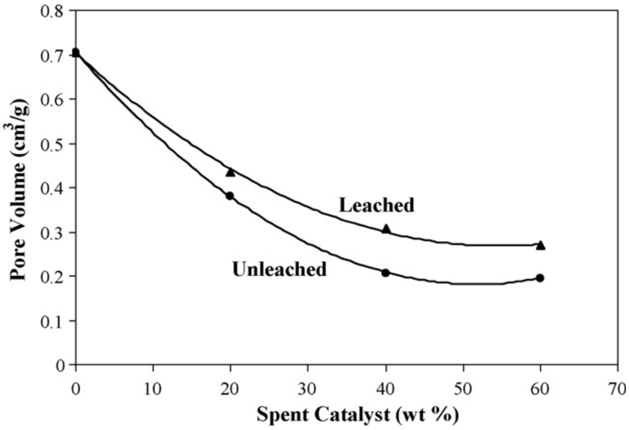

Fig. 4. Pore volume comparison between the catalysts prepared from leached and unleached spent catalysts.

Higher surface area and pore volume values are observed for the catalysts prepared with the spent catalysts with leaching. Although, the surface area and pore volume values decrease progressively with increase in the amount of spent catalyst mixed with boehmite in both cases, the decline in the surface area and pore volume is relatively low when a part of the metals in the spent catalyst is removed by leaching before mixing the spent catalyst with boehmite. This is not surprising since leaching of the deposited metals such as V and Ni from the spent catalyst opens up the pores and increases the pore volume and surface area.

The HDS and HDV activities of the catalysts prepared from leached and unleached spent catalyst are compared in Fig. 5a and b, respectively. The results clearly show that the catalysts prepared from MLSC are more active than those prepared with unleached spent catalyst. This high activity could be attributed to the lower vanadium content and higher surface area and pore volume of the catalyst prepared MLSC. This point is explained in more detail in a later section dealing with discussion of the results.

3.2. Characteristics and HDM/HDS activities of the catalysts prepared using HTSC

The spent catalyst was subjected to hydrothermal treatment in an autoclave at 300 °C for 2 h. The treated catalyst was dried and characterized. The pore volume and pore size distribution of the spent catalyst before and after hydrothermal treatment are compared in Fig. 6. It is seen that the total pore volume of the catalyst is increased form 0.24 to 0.48 ml/g by hydrothermal treatment. The surface area also increased substantially (from 37 to 70 m^2/g). A comparison of the pore size distribution data of the spent catalyst before and after hydrothermal treatment clearly shows that enlargement of pores has occurred by hydrothermal treatment. The volume of pores in the 100–2000 Å diameter range is increased remarkably (from 0.16 to 0.38 ml/g). Particularly, the mesopore volume in the 100–500 Å diameter is increased by

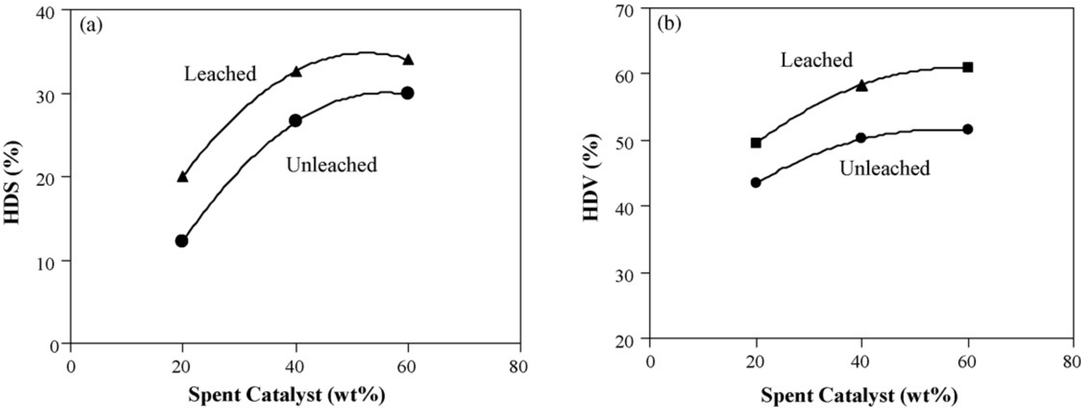

Fig. 5. HDS and HDV activity comparison at 370 °C between the catalysts prepared from leached and unleached spent catalysts: (a) HDS and (b) HDV.

from 0.12 to 0.24 ml/g and the volume of medium large pores in the 500–2000 Å range is increased from 0.02 to 0.12 ml/g.

The HTSC sample was mixed with boehmite in different ratios (i.e. 20%, 40% and 60%) and then extruded. Similar preparations were also made using the spent catalyst without hydrothermal treatment. The catalyst extrudates were then characterized after drying and calcinations. The surface area and pore volume data for the catalysts prepared by mixing different percentages (20%, 40% and 60%) of HTSC are compared with that of the catalysts prepared from the untreated spent catalyst in Fig. 7a and b. The results show that the catalysts prepared by mixing HTSC with boehmite have higher surface area and pore volume than those prepared from the spent catalyst without hydrothermal treatment. For example, for the catalyst prepared by mixing 40% of spent catalyst, without hydrothermal treatment, the surface area and pore volume values are 70 m^2/g and 0.27 ml/g, respectively, whereas for the catalyst prepared from the same amount of HTSC, the surface area and pore volume are, respectively, 144 m^2/g and 0.39 ml/g.

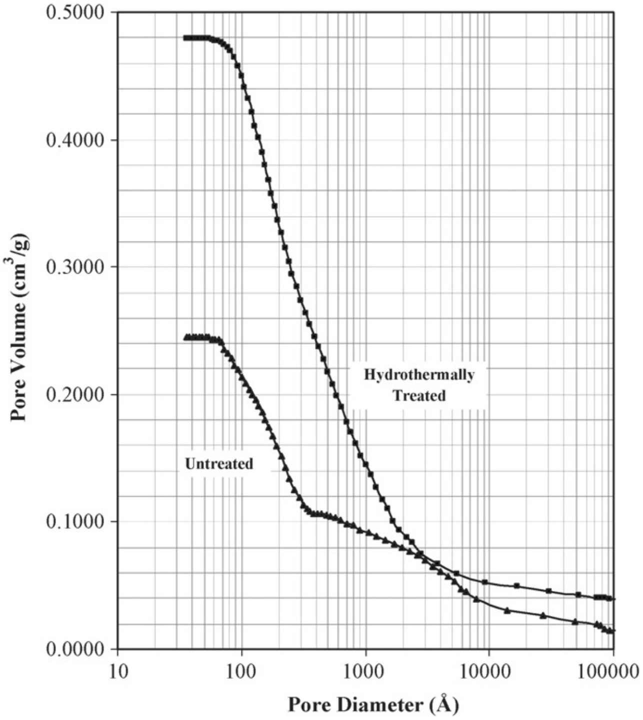

Fig. 6. Effect of hydrothermal treatment on pore size distribution of spent catalyst.

In Fig. 8, the HDS and HDV activities of two catalysts, one prepared by mixing 40 wt% of the spent catalyst (without hydrothermal treatment) with boehmite and the other prepared from the same percentage of HTSC mixed with boehmite, are presented. The HDS and HDV activities of a commercial HDM catalyst tested under similar conditions is also included in the same figure for the purpose of comparison.

The results show that the catalyst prepared from the spent catalyst which was subjected to hydrothermal treatment is more active than that prepared from the spent catalyst without hydrothermal treatment for promoting HDS and HDM reactions in residual oil hydrotreating. It is interesting to note that the catalysts prepared from both types of spent catalysts are more active than the reference HDM catalyst.

4. Discussion

Catalysts used in the hydroprocessing of petroleum residues are deactivated by coke and metal deposits originating from the heavy feedstock [16–18]. The foulant metals are usually concentrated near the outer surface of the pellet, blocking pore mouths and reducing markedly the active surface area available within the inner pores of the catalyst [42]. In the decoked spent catalyst, although the carbon deposit is removed completely, the metallic impurities remain on the catalyst and act as a diffusion barrier for the reactants. Leaching of the deposited metals from the pores can open the pores. Previous experiments in this laboratory on the distribution profiles of vanadium in the spent catalyst before and after leaching showed that a substantial amount of vanadium accumulated near the outer edge of the pellet blocking the pore mouths was removed by acid leaching and thereby, increased the pore volume and surface area [39]. The extent of surface area and pore volume recovery by metal-leaching treatment was found to increase with increasing vanadium extraction from the spent catalyst. Increase in surface area and pore volume was substantially high

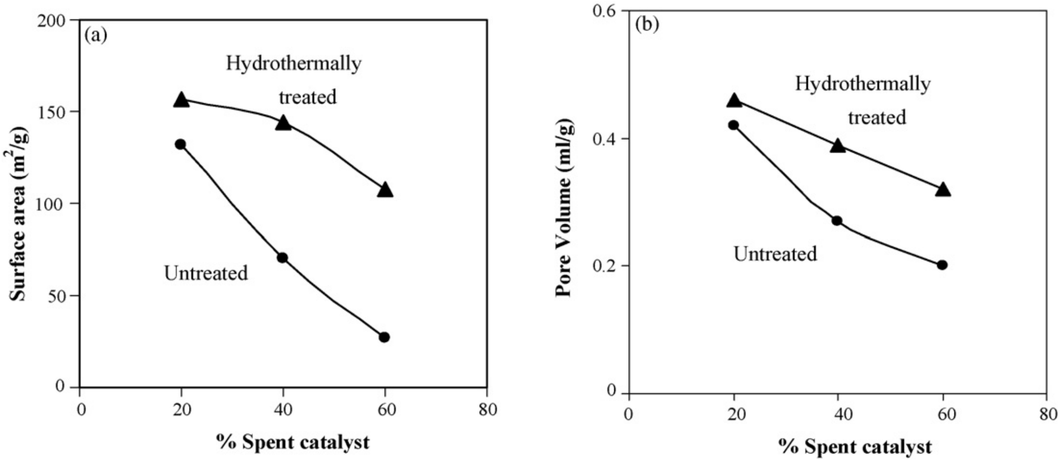

Fig. 7. Comparison of surface area and pore volume values of catalysts prepared from the spent catalysts with and without hydrothermal treatment: (a) Surface area and (b) pore volume.

up to about 30% vanadium removal. The larger surface area and pore volume values of the catalysts prepared from leached catalysts and their higher HDS and HDM activities are consistent with the above results.

The larger surface area and pore volume values of the catalysts prepared from HTSC and their higher HDS and HDM activities can be explained as follows. Hydrothermal treatment leads to enlargement of pores in the catalyst, a previous study [43] in this laboratory showed that conversion of γ-alumina to boehmite occurs during hydrothermal treatment. The conversion of γ-alumina to boehmite essentially involves rehydration of γ-alumina to boehmite by the uptake of 1 mol of H_2O per mole of Al_2O_3 according to the following scheme.

$$\underset{\gamma-\text{alumina}}{Al_2O_3} \xrightarrow{H_2O} \underset{\text{boehmite}}{2AlO(OH)}$$

The boehmite formed from γ-Al_2O_3 by hydrothermal treatment was found to be well crystallized with large crystallites by X-ray diffraction analysis. Calcination of the large crystallite size boehmite at 500 °C in air could be expected to result in the formation of γ-Al_2O_3 with large pores.

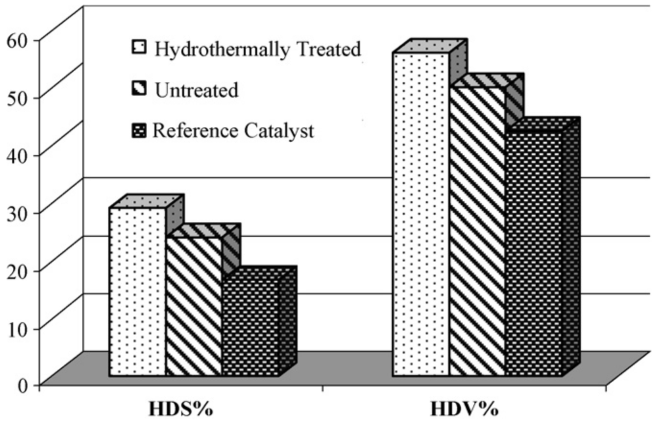

Fig. 8. Comparison of the HDS and HDV activities of a reference HDM catalyst with that of catalysts prepared from hydrothermally treated and untreated spent catalysts.

In alumina supports, porosity originates from the space between the particles [44]. When alumina particles with large crystallite size are packed to form extrudates, the space between the particles (i.e. pore size) will be large. Therefore, rehydration of γ-alumina present in the spent catalyst and its transformation to well-crystallized boehmite could be responsible for the enlargement of pores. The higher surface area of the hydrothermally treated catalyst could be attributed to the increase in the volume of the mesopores in the catalyst.

The results of the present studies show that highly active catalysts for residual oil hydrotreating could be prepared from spent $NiMo/Al_2O_3$-type catalysts containing high levels of vanadium deposit by subjecting them to acid-leaching or hydrothermal treatment. Up to 60 wt% of spent catalyst could be mixed with boehmite in the case of treated spent catalysts for preparing catalysts with substantial HDS and HDM activities. The scientific basis for the high hydrotreating activities of these catalysts is explained below.

Catalysts used for hydrotreating of petroleum distillates and residues normally consist of Mo supported on an alumina carrier with promoters such as Ni or Co [45]. Mo alone can promote hydrotreating reactions such as HDS and HDM, but its activity is enhanced by the presence of Ni or Co. The synergy between Mo and Ni in promoting hydrotreating reactions has been explained on the basis of the formation of an active phase (Ni–Mo–S) which contains both metals [45,46].

Conventional HDM catalysts contain 4–6% MoO_3 either alone or together with 0.5–1% NiO on a large pore (140–170 Å diameter) alumina support. These catalysts possess low intrinsic HDM activity and proper porosity to allow the large metal-bearing molecules to reach the active sites within the catalyst pores. In the catalysts prepared by mixing spent residue hydrotreating catalysts with boehmite, vanadium is present together with Mo and Ni. Close association between the three metals (V, Mo and Ni) in different combinations could also occur in the spent and prepared catalysts. Dejonghe et al. [47] found that in Ni–Mo–S/Al_2O_3 catalysts Ni can be, at least, partly replaced by V coming from the feed during residual oil hydrotreating process. Smith and Wei [48] speculated that in residual oil hydrotreating catalysts aged by the deposition of V and Ni, new active catalyst surface could be formed. Sie [49] and Devanneaux et al. [50] found that the deposited Ni and V in the form of sulfides can themselves act as catalysts for metal removal reactions. Takeuchi et al. [51] demonstrated bare alumina carriers gradually acquired catalytic activity for HDM by the deposition of metals (V and Ni) during hydrotreatment of residual oils. Sasaki et al. [52] reported that NiV/Al_2O_3 catalysts had comparable activity as CoMo/Al_2O_3 for demetallization of residues. Recently, Betancourt et al. [53] observed a synergy effect in mixed vanadium–nickel sulfides for promoting hydrotreating reactions. Many other studies have shown that V either alone or in combination with Ni or Mo is very efficient for the HDM process [54–56]. Therefore, it is highly likely that some kind of new active sites formed from V, Mo and Ni are responsible for the high activity of the catalyst prepared from spent catalyst.

In the spent catalyst, the deposited vanadium is more concentrated near the outer surface of the catalyst pellet plugging the pores and reducing the catalyst's surface area and porosity. In the acid-leached spent catalyst, the vanadium is removed from the pore mouths and the surface area and porosity of the catalyst are improved. In the case of hydrothermal treatment pore enlargement occurs with an increase in the surface area and pore volume. As a result, the catalysts prepared from the treated catalysts have large surface area and pore volume. Thus, the presence of some new kind of active sites formed from V, Mo and Ni in the catalysts prepared from the spent catalysts together with their high surface area and porosity could be responsible for their higher hydrotreating activity. More research is needed to develop a fundamental understanding of the nature of active sites in catalysts containing mixed sulfides of V, Mo and Ni.

5. Conclusions

This study deals with the utilization of spent residue hydroprocessing catalysts, which contained high levels of vanadium, in the preparation of active new hydrodemetallization catalyst compositions. The metal fouled-spent catalyst with very low surface area and pore volume was subjected to metal-leaching or hydrothermal treatment to reduce the fouling effect of vanadium and then mixed and extruded with boehmite to prepare new catalysts extrudates. The prepared catalysts were characterized and their activities for promoting HDM and HDS reactions were evaluated by hydrotreating tests using Kuwait atmospheric residue as feed. The following are the important results and conclusions of the study:

- Catalyst prepared by mixing the MLSC with boehmite had higher surface area and pore volume and showed higher hydrotreating activity than that prepared from unleached spent catalyst. Removal of vanadium blocking the pores of the catalyst by acid leaching was responsible for improved surface area and porosity.
- Hydrothermal treatment of the spent catalyst increased its porosity and surface area by transforming the γ-Al_2O_3 present in the spent catalyst to well-crystallized boehmite. Catalysts prepared from HTSC had higher surface area and pore volume and showed higher HDM and HDS activities than that prepared from the spent catalyst without hydrothermal treatment.
- The catalysts prepared from the treated spent catalysts also exhibited substantially higher HDM and HDS activities than the reference commercial HDM catalyst.
- Larger amounts (40–60 wt%) of spent catalyst can be added to boehmite in the case of treated spent catalysts for preparing new catalysts with large pores, fairly high surface area and pore volume, and high activity for promoting HDM and HDS reactions.
- Spent catalysts with high levels of vanadium can be recycled and their environmental problem can be minimized by utilizing them in the preparation of active new catalyst compositions containing V, Mo, Ni and Al_2O_3 for residual oil hydrodemetallization.

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References

[1] M. Absi-Halabi, J. Beshara, H. Qabazard, A. Stanislaus, Catalysts in Petroleum Refining and Petrochemical Industries, Elsevier, Amsterdam, The Netherlands, 1996.

[2] P. Leprince, Petroleum Refining, vol. 3-Conversion Processes, Technip, Paris, 2001.

[3] M. Absi-Halabi, A. Stanislaus, H. Qabazard, Hydrocarbon Process. (February) (1997) 45–55.

[4] K.G. Knudsen, B.H. Cooper, H. Topsoe, Appl. Catal A: Gen. 189 (1999) 205.

[5] I.V. Babich, J.A. Moulljn, Fuel 82 (2003) 607.

[6] M. Breysse, G. Diega-Mariadassou, S. Pessayre, G. Geantet, M. Vrinet, M. Lemaire, Catal. Today 84 (2003) 129.

[7] C. Song, X. Ma, Appl. Catal. B: Environ. 41 (2003) 2007.

[8] M.R. Gray, Upgrading Petroleum Residues and Heavy Oils, Marcel Dekker, New York, 1994.

[9] J.F. LePage, Resid and Heavy Oil Processing, Technip, Paris, 1992.

[10] J.G. Speight, Desulfurization of Heavy Oils and Residues, Marcel Dekker Inc., New York, 2000.

[11] R.P. Silvy, Appl. Catal. 261 (2004) 247.

[12] S. Kressmann, F. Morel, V. Harle, S. Kasztelan, Catal. Today 43 (1998) 203.

[13] E. Furimsky, Appl. Catal. A: Gen. 171 (1998) 177.

[14] T.M. Oelderik, S.T. Sie, D. Appl. Catal. 47 (1990) 1.

[15] A. Marafi, S. Fukase, M. Al-Marri, A. Stanislaus, Energy Fuels 17 (2003) 661.

[16] K. Al-Dalama, A. Stanislaus, Chem. Eng. J. 120 (2006) 33.

[17] E. Furimsky, F.E. Massoth, Catal. Today 52 (1999) 381.

[18] D.L. Trimm, Stud. Surf. Sci. Catal. 53 (1990) 41.

[19] D.L. Trimm, Appl. Catal. A: Gen. 212 (2001) 153.

[20] E. Furimsky, Catal. Today 30 (1996) 223.

[21] D. Rapaport, Hydrocarbon Process. 79 (2000) 11.

[22] United State Environmental Protection Agency (USEPA), Hazardous Waste Management System, Federal Register vol. 68, No. 202, 2003, p. 59935.

[23] M. Marafi, A. Stanislaus, J. Hazard. Mater. B 101 (2003) 123.

[24] T. Chang, Oil Gas J. (October 9) (1998) 79.

[25] R.K. Clifford, Spent catalyst handling, Petrol. Technol. Quart. (1997) 33.

[26] Y. Chen, Q. Feng, Y. Shao, G. Zhang, L. Qu, Y. Lu, Miner. Eng. 19 (2006) 94.

[27] B.B. Kar, P. Datta, V.N. Misra, Hydrometallurgy 72 (2004) 87.

[28] R.J. Schreiber, Jr., C. Yonley, The use of spent catalyst as a raw material substitute in cement manufacturing. Symposium on Regeneration, Reactivation and Reworking of Spent Catalysts presented before the Division of Petroleum Chemistry, Inc., 205th National Meeting, American Chemical Society, Denver, CO, (March 28–April 2) 1993.

[29] D.D. Sun, J.H. Tay, H.K. Cheong, D.L.K. Leung, G.R. Qian, J. Hazard. Mater. 87 (2001) 213.

[30] M. Lee, R.D. Kundsen, D.R. Kidd, Ind. Eng. Chem. Res. 31 (1992) 487.

[31] E. Furimsky, Appl. Catal. A: Gen. 156 (1997) 207.

[32] K. Choi, K. Lee, S. Ho, C. Woo, J. Seong, US Patent 6,673,740 (2004).

[33] M. De Boer, US Patent 6,030,915 (2000).

[34] Gardner, E.K. Lloyd, R. Dennis, US Patent 4,888,316 (1989).

[35] M. Marafi, A. Stanislaus, M. Absi-Halabi, Appl. Catal. B: Environ. 4 (1994) 19.

[36] M. Marafi, E.K.T. Kam, A. Stanislaus, A novel process for recycling spent hydroprocessing catalyst: an economic analysis, in: Presented at the 16th World Petroleum Congress, Calgary, Canada, June 11–15, 2000.

[37] A. Stanislaus, M. Marafi, M. Absi-Halabi, Appl. Catal. A: Gen. 105 (1993) 195.

[38] M. Marafi, A. Stanislaus, J. Mol. Catal. A: Chem. 202 (2003) 117.

[39] A. Stanislaus, M. Marafi, M. Absi-Halabi, Residual oil hydrotreating catalyst rejuvenation by leaching of foulant metals: effect of metal leaching on catalyst characteristics and performance, in: M.L. Occelli, R. Chianelli (Eds.), Hydrotreating Technology for Pollution Control, Macel Dekker, New York, 1996, p. 327.

[40] M. Marafi, A. Stanislaus, Catal. Lett. 18 (1993) 151.

[41] M. Marafi, A. Stanislaus, A. Al-Barood, S. Al-Omani, H. Al-Sheeha, Ind. Eng. Chem. Res. 46 (2007) 1968.

[42] R.J. Qann, R.A. Ware, C.W. Hung, J. Wei, Adv. Chem. Eng. 14 (1998) 95.

[43] A. Stanislaus, K. Al-Dalama, M. Absi-Halabi, J. Mol. Catal. A: Chem. 181 (2002) 33.

[44] D.L. Trimm, A. Stanislaus, Appl. Catal. 21 (1986) 215.

[45] H. Topsoe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis Science and Technology, Springer, Berlin, Germany, 1996.

[46] J.A.R. Van Veen, H.A. Colign, P.A.J.M. Hendriks, A.J. Van Welsenes, Fuel Process. Technol. 35 (1993) 137.

[47] S. Dejonghe, R. Huban, J. Grimblot, J.P. Bonnelle, T. Faure, Catal. Today 7 (1990) 569.

[48] J.B. Smith, J. Wei, Deactivation in Catalytic Hydrodemetallization, J. Catal. 132 (1991) 1.

[49] S.T. Sie, in: B. Delmon, G.F. Froment (Eds.), Stud. Surf. Sci. Catal., vol. 6, Elsevier, Amsterdam, 1980, p. 545.

[50] J. Devanneaux, J.P. Gallex, P.A. Engelhard, ACS Prepr. Div. Petrol. Chem. 30 (1985) 84.

[51] C. Takeuchi, S. Asaoka, S. Nakata, Y. Shiroto, ACS Prepr. Div. Petrol. Chem. 30 (1985) 96.

[52] Y. Sasaki, Y. Ojima, T. Kondo, K. Ukegawa, A. Matsumura, T. Sakabe, J. Jpn. Petrol. Inst. 25 (1982) 27.

[53] P. Betancourt, A. Rives, C.E. Scott, R. Hubaut, Catal. Today 57 (2000) 201.

[54] R.L.C. Bonne, P. Van Steenderen, J.A. Moujiin, Bull. Sic. Chim. Belg. 100 (1991) 877.

[55] R. Marseu, G. Martino, J.C. Plumail, Influences of nature of active phases on the catalytic activity and on the evaluation of asphaltenes and resins during hydrotreating of Boscan crude, in: M.J. Philips, M. Ternam (Eds.), Proceedings of the 9th International Congress on Catalysis, vol. 1, Chemical Institute of Canada, Ottawa, 1988, p. 144.

[56] J.P. Jansons, V. Langeveld, J.A. Moulijin, Appl. Catal. A: Gen. 179 (1999) 229.