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Long-term evaluation of NiMo/alumina–carbon black composite catalysts in hydroconversion of Mexican 538 °C+ vacuum residue

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Abstract

Alumina with (8–18 wt.%) carbon black composite (AMAC) supports was prepared as bimodal extrudates, containing 11–20% of total pore volume as macropores (i.e. >1000 Å). These supports, in spite of containing carbon black and macropores, showed good side crushing strength (0.67–1.19 kg/mm) after pyrolysis in 6% O_2/N_2. AMAC-catalysts were obtained after impregnating these alumina–carbon black supports with Ni and Mo, to obtain 3.5 wt.% NiO and 15 wt.% MoO_3. These catalysts were evaluated for about 700 h in the hydroconversion of a Mexican vacuum residue (538 °C+) at 415 °C, 200 kg/cm^2, H_2/HC = 6000 ft^3/barrel in a pilot plant equipped with a Robinson–Mahoney reactor. In comparison with a commercial bimodal alumina-based catalyst (ComCat), AMAC catalysts showed much fewer sediments and less Conradson carbon formation. Initial HDS in AMAC containing macropores can be as high as 92%, while that in a ComCat is 86%. On average, yields of naphtha and kerosene were 2.6 and 1.34 times higher with AMAC catalysts than those with ComCat, while diesel yields were similar.

Keywords: Hydroconversion; Hydrodesulfurization; Hydrodenitrogenation; Vacuum residue; H-oil; Carbon-black; Alumina support; Macropores

1. Introduction

Petroleum residues are the heavy fraction remaining after distilling petroleum crudes at atmospheric pressure (atmospheric residue) or at reduced pressure of 25–100 mmHg (vacuum residue). Residues have high molecular weight ($\gg$1000 amu number average for vacuum residue) and contain polynuclear aromatics, also termed asphaltenes. Because of their high thermal stability, asphaltenes having 3–4 rings provide the greatest limitation to the conversion of residue. In addition, the high concentrations of heteroatoms (sulfur, nitrogen, vanadium, and nickel) in petroleum residue act along with asphaltenes to poison catalysts. No matter which type of process is used, a substantial fraction of residue molecules can be cracked off as fragments to become liquids in the transportation fuel and vacuum gasoil boiling ranges. However, one should not try to overly convert residues because asphaltene content can force the selectivity to go to the thermodynamically favored, but lower valued, products: coke and/or sediments and/or hydrocarbon gases. One of the processes designed to convert heavy oil residue to lighter fractions is the so-called H-Oil^{TM}, which typically operates at 410–420 °C, 120 kg/cm^2, LHSV: 0.5 h^{-1}, H_2/HC: 3500 ft^3/barrel, and uses an ebullated bed reactor.

Maya crude oil is classified as heavy oil, and it accounts for more than 50% of the total crude oil production in Mexico. In terms of environmental problems, catalytic hydrodesulfurization (HDS) and hydrocracking (HC) technologies are important to produce low sulfur fuel oils by upgrading residues from Mexican crude oil which contain not only high concentrations of sulfur compounds (around 4.5 wt.%), and catalyst-deactivating vanadium compounds (around 400 ppm), but also asphaltenes. At present, Mexican refineries operate with crude oil blends, that is, 55–60% Isthmus (e.g., the Mexican light blend), and 45–40% Maya (e.g., the Mexican heavy blend) crude oils; but since heavy oils tend to become relatively abundant, an unavoidable situation for the Mexican oil industry in the near future will be to refine Maya crude oil richer blends. Two H-Oil^{TM} plants, which have been operating for more than 30 years in the Salamanca, Gto. refinery (18,500 BPD designed capacity), and more recently in the Tula, Hgo. refinery (50,000 BPD designed capacity), transform Mexican heavy vacuum residue into more valuable oil fractions, such as gasoil and diesel, removing great amounts

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of polluting sulfur compounds. Nonetheless, the H-Oil^{TM} process is frequently hampered by the formation of high-molecular weight compounds, called sediments, which cause many downstream operational problems, especially by blocking valves, pumps, flow-control devices, and hot and cold separators. Sediments are polynuclear aromatics which result from complex cracking, recombination, and nucleation reactions among asphaltenes [1]. H-Oil^{TM} plants cannot operate at high conversion levels since sediment yields rise, particularly when using heavy residue from heavy crude oils [2]. Thus, sediment yields above 1 wt.% render H-Oil^{TM} plant operation anywhere from troublesome to inoperable. Taking into account these drawbacks, new catalyst designs must offer: (1) accessibility to large asphaltene agglomerates in order to increase their diffusion and transformation, and (2) catalytic active sites or support adsorption sites that are less favorable to sediment formation.

In the first approach, and to overcome the difficulty of asphaltene diffusion through small pores, an appropriate porous structure can be obviously rationalized in terms of creating macropores (>1000 Å) in the shaped support or catalyst. However, not that many macropores (ca. above 30% of total pore volume) should be created, since shaped particles could turn fragile. The formation of macropores in extrudates is a direct consequence of support or catalyst formulation when making extrudates. In fact, new generation commercial catalysts developed for the H-Oil^{TM} process contain macropores [3]. The second approach deals with the catalyst support's intrinsic acid sites (e.g., γ-Al_2O_3) [4], which are believed to participate in sediment formation.

In this study, an alumina–carbon black composite support was developed with the aim of diminishing either the strength, and/or number of acid sites. Carbon black: (i) is cheap, (ii) has a low tendency to form coke-related compounds (e.g., very weak acid sites), (iii) has an affinity for V and Ni porphyrine-like compounds, which could be refrained from attacking catalytic active sites, (iv) has high hydrodesulfurization (HDS) [5,6] and hydrodenitrogenation (HDN) [6–8] activity, and (v) has no micropores below 30 Å which could be easily occluded, therefore turning active Ni and Mo metals into inactive ones. In earlier works, microporous activated carbon was used as a support, despite the fact that micropores are of little use for catalytic reactions involving large molecules [9], and it is more expensive than carbon black. Unfortunately, carbon or carbon black supports are known for their low mechanical resistance; this physical property being of the utmost importance since shaped catalyst particles will be colliding among themselves and against reactor walls in the ebullated bed reactor. On the other hand, pyrolyzed carbon, or pyrolyzed carbon black, has good mechanical properties. Very little work has been reported on the hydroconvertion of heavy residues on NiMo- or CoMo- catalysts based on carbon supports. For instance, Segawa et al. used NiMo on active carbon as a catalyst for the hydrogenation of an Arabian vacuum residue, and they found that coke formation was considerably suppressed [10].

One of the challenges of this study is to achieve an intimate and homogeneous mixture of Al_2O_3 and carbon black in an extrudable paste, which could eventually result in macropore-containing, mechanically resistant, Al_2O_3–carbon black extrudates. In order to record deactivation, using near real-operation conditions, selected catalysts, obtained from impregnating these prospective supports simultaneously with Ni and Mo, were evaluated and monitored continually for about 700 h on the run. A bimodal alumina-based NiMo commercial catalyst was used as a comparison.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Support preparation

Catalysts were prepared by closely following the preparation procedure shown in Fig. 1. Commercial boehmite-phase alumina (325 m^2/g; acid dispersability index: 30%; loose bulk density: 192–224 kg/m^3; $Na_2O < 0.01$ wt.%), dried at 110 °C, was used throughout the study. This alumina (200 g) was kneaded with 1–1.5vol.% acetic acid (280–320 cm^3) for about 30 min. Then, 15 g of carbon black #970 (particle size: 16 nm, specific surface area: 260 m^2/g), from Mitsubishi Chemicals, and sucrose (15 g), used as a binder, were poured in, after which kneading continued for about 15 min. The black wet paste obtained was kept in a closed plastic vessel for 12 h at room temperature, in order to maintain moisture and allow homogenization of the mixture. Then, the paste was extruded in a Brabender mechanical extruder at a constant speed (30 rpm), using 1/16 in. dice. Wet extrudates were

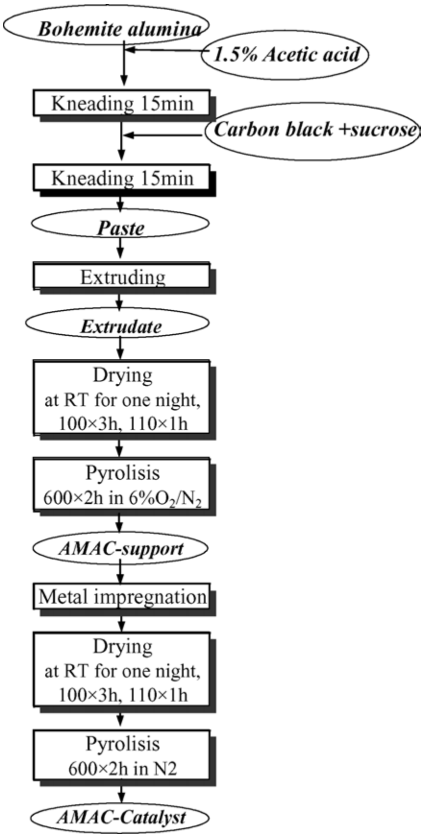

Fig. 1. Preparation scheme of AMAC supports and catalysts.

allowed to dry at room temperature overnight, after which they were dried at 100 °C for 3 h, and 110 °C for 1 h in a static oven. After this, the cylindrical-shaped particles were transferred to a tubular oven and were heat-treated in flowing 6 vol.% O_2/N_2, where the temperature was increased 5 °C/min and then remained at 600 °C for a period of 2 h. The activated black extrudates were then impregnated with Ni and Mo. Hereinafter, AMAC, which stands for alumina modified with amorphous carbon black, will be the term used to refer to these supports.

2.1.2. *Ni and Mo impregnation*

First, an aqueous ammonia ($NH_4OH + H_2O$ 3:1) solution of $[Ni_5(CO_3)_2\ (OH)_6{\cdot}4H_2O]$ and MoO_3 was prepared, in order to obtain 3.5 wt.% NiO and 15 wt.% MoO_3 on an 81.5 wt.% dried AMAC support. The amount of solution was calculated as 80% of the total pore volume, determined by water absorption, i.e., the incipient wetness technique. This metals solution was evenly sprayed by means of an atomizer, onto the shaped support in a rotary impregnation vessel. Then, the impregnated extrudates were dried for 12 h at room temperature, at 100 °C for 3 h, 110 °C for 1 h, and finally heat-treaded in flowing N_2 where the temperature was increased 5 °C/min and then remained at 600 °C for a period of 2 h. These catalysts will be referred to as AMAC catalysts.

2.2. *Characterization*

Pore-size distribution and pore volume of support and catalysts were determined by a Quantachrome Autoscan Hg-porosimeter, using samples previously dried at 120 °C for 4 h. Total pore volume, defined as water-holding capacity, was measured as maximum water absorbed into a dry support or catalyst. The size (i.e., length and diameter) of the support and catalysts was measured using an electronic digital clipper, and the side crushing strength (SCS) was automatically measured using a Seiko-Kyowa KA-300PB precise Rheorobot, closely following the ASTM DD4179-01 method. The amount of carbon black incorporated into a support was determined via the gravimetric method by burning at 600 °C, 2 h in air; samples were previously heat-treated in 6% O_2/N_2, as indicated in the support preparation section. Loss-on-attrition was measured as follows: after stirring 50 g of extruded catalyst in 500 g of diesel for 8 h at 100 rpm and room temperature in a stainless steel beaker, all the particles that passed through mesh #20 were quantified and recorded as wt.%.

2.3. *Evaluation*

Feedstock was a vacuum residue (ca. 80%) made up of a mixture of 60% Isthmus and 40% Maya crude oils, and vacuum gasoil cutback (ca. 20%) characterized by physico-chemical properties shown in Table 1.

Evaluation of a commercial alumina-based bimodal catalyst (ComCat) and AMAC-based catalysts was carried out in a pilot plant equipped with a Robinson–Mahoney reactor, where catalysts were loaded in a 316SS meshed basket attached to the stirring shaft. Once the reactor was set up, pre-sulfiding of the catalyst was carried out by flowing 1 wt.% CS_2 in naphtha (150 cm^3/min) and H_2 (76 l/h) under a total pressure of 30 kg/cm^2, and stirring rate of 300 rpm. The reactor temperature was gradually increased in 50 °C steps and held for 6 h until reaching 300 °C. After this, the reactor pressure was increased to 200 kg/cm^2 and vacuum residue was fed at 50 cm^3/h instead of naphtha; then, the reactor temperature rose to 330 °C for 12 h and the H_2 supply rate was 76 l/h. Afterward, temperature was gradually increased in approximately 20 °C steps and maintained for 12 h until reaching 415 °C, and after 24 h, stationary operations began and samplings were taken every 24 h. Reaction conditions were fixed as follows: reaction temperature, 415 °C; pressure, 200 kg/cm^2; LHSV, 0.5 h^{-1}; H_2/hydrocarbon, 6000 ft^3/barrel; total time-on-run, 600–700 h.

Table 1
Composition and properties of feedstock

Maya residue + VGO cut back	
Sulfur (wt.%)	5.68
Nitrogen (wppm)	5136
Nickel (wppm)	69.1
Vanadium (wppm)	345.9
Sediment (wt.%)	0.05
n-C7 insoluble (wt.%)	15.65
CCR (wt.%)	20.78
Gravity, 20/4 °C	1.0327
API	3
Dist. IBP	425.5
5%	499
10%	530.5
20%	571
30%	609.5
40%	655.5
50%	719
Yield (wt.%)	
Gasoil	19.76
Residue	80.24

2.4. *Product analysis.*

Total sediments in the liquid product were determined following the ASTM D4870-99 method. Ni and V in the liquid product were determined by the ASTM D5863 method using atomic absorption on a Perkin-Elmer PE5000 spectrophotometer. Yields to different hydrocarbon fractions were measured by simulated distillation in an Agilent 6890N gas chromatograph, following the ASTM D5307 method. Total sulfur in the liquid product was quantified in an X-ray Horiba SLFA1800 apparatus, following the ASTM4294 method. Total nitrogen was measured in an Antek9000, following the ASTM4629 method. Conradson carbon residue (CCR) was determined following the ASTM D189 method.

3. Results and discussion

A general preparation of the AMAC supports and catalysts used in this study is shown in Fig. 1, where the most distinctive and noteworthy aspects are the addition of carbon black and the near-pyrolysis conditions (6 vol.% O_2/N_2) in the heat-treatment. Numerous attempts to obtain bimodal alumina-carbon composites were pursued by using different carbon sources such as polyvinyl alcohol and furfuryl alcohol, as well as different peptizing/agglomerating additives, such as HNO_3, NH_4OH, acetic acid, sucrose, starch, and methyl-cellulose, all in different amounts and combinations. Nevertheless, most of the resulting extrudates were not made up of macropores. The best results were obtained when combining acetic acid and the indicated amounts of carbon black. Since an oxidizing atmosphere burns off carbon, all heat-treatments were carried out in 6 vol.% O_2/N_2, while carbon-loss at this condition was neglected. A little O_2 aids in removing volatile components (e.g., water) without removing carbon. Accordingly, carbon blacks exhibit a high reactivity towards polymerization under weakly oxidizing conditions; the cross-linking of carbon stacks results in non-graphitizable hard carbon black [11].

Some relevant properties of AMAC supports and catalysts are given in Table 2. AMAC-117 shows no macroporosity, and it was chosen as a comparison for the other AMACs. Notice that macroporous AMACs are on average 38% less mechanically resistant than the one without macropores (AMAC-117). As mentioned above, a compromise between macropore formation and mechanical strength is crucial. Macropores are between 14 and 22% of the total pore volume, measured by Hg-porosimetry. After Ni and Mo impregnation, AMAC catalysts were obtained, and their physical properties are shown in the lower part of Table 2. A comparison of side crushing strength values between catalysts and supports revealed that some catalysts (AMAC-117 and -128) increased their mechanical resistance between 50 and 25%, probably because of metals contribution; the other AMACs remained practically unchanged. A relative number of macropores remained near the one belonging to the related support, or rather, between 20 and 24% of the total pore volume, suggesting that metals impregnation was sufficiently uniform to allow meso and macropores to remain unplugged. Pore-size distribution of AMAC catalysts, which is essentially the same as that of AMAC supports, is shown in Fig. 2. Bimodal characteristics of AMAC catalysts are evident, with macropore average values of AMAC supports being 1400, 2600, 3500, and 3670 Å, depending on the formulation conditions. For clarity, pore-size distribution of AMAC-117 was not included in Fig. 2, but it contains only mesopores, as indicated in Table 2.

An evaluation of AMAC catalysts was carried out selecting a unimodal AMAC-117 and two bimodals, AMAC-128 and -142, in order to examine possible contributions of macropores, and they were all compared with ComCat. Stability of pilot plant operation was good in terms of reaction temperature 415 ± 5 °C (see Fig. 3) and average LHSV 0.54 ± 0.02 to 0.60 ± 0.04 (see Fig. 4), except for AMAC-128 where LHSV

Table 2
Properties of ComCat and AMAC-based supports and catalysts

	ComCat	AMAC-117	AMAC-128	AMAC-137	AMAC-142	AMAC-145
Support						
Shape	Cylindrical	Cylindrical	Cylindrical	Cylindrical	Cylindrical	Cylindrical
Diameter (mm)	un	1.39	1.33	1.4	1.41	1.39
SCS (kg/mm)	un	1.19	0.73	0.71	0.84	0.67
Pore volume (cm^3/g)						
Total	un	0.64	0.79	0.92	0.89	0.90
Meso (<1000 Å)	un	0.64	0.68	0.72	0.70	0.70
Macro (>1000 Å)	un	0.200	0.11	0.20	0.19	0.20
Pore peaks (Å)	un	93	100, 1400	102, 3500	95, 2600	97, 3670
Total pore volume[a] (cm^3/g)	un	0.72	0.85	1.00	0.90	1.00
Carbon content (wt.%)	un	13.40	13.10	8.49	10.50	11.60
Catalyst						
Diameter (mm)	1.07	1.19	1.35	1.44	1.40	1.40
SCS (kg/mm)	0.72	1.78	0.91	0.68	0.74	0.70
Pore volume (cm^3/g)						
Total	0.75	0.5	0.65	0.73	0.71	na
Meso (<1000 Å)	0.59	0.5	0.52	0.55	0.55	na
Macro (>1000 Å)	0.16	0.00	0.13	0.18	0.16	na
Pore peaks (Å)	121, 3600	113	102, 1450	114, 3570	108, 2690	na
Total pore volume[a] (cm^3/g)	0.80	0.61	0.70	0.79	0.75	0.80
Carbon content (wt.%)	–	11.1	10.1	8.2	9.5	10.2
NiO (wt.%)	3.5	3.5	3.5	3.5	3.5	3.5
MoO_3 (wt.%)	14.5	15.0	15.0	15.0	15.0	15.0
CaO (wt.%)	–	0.0	0.0	1.6	1.6	0.8
CBD	0.58	0.5	0.56	0.52	0.53	0.51
Attrition loss (wt.%)	3.9	2.5	3.0	3.3	na	na

ComCat: NiMo on alumina-based commercial catalyst, SCS: side crushing strength, CBD: catalyst bulk density; un: unavailable, na: not analyzed.

[a] Measured by water absorption.

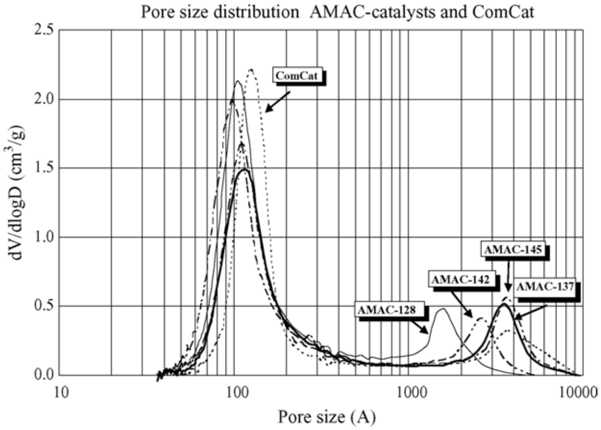

Fig. 2. Pore-size distributions of AMAC and ComCat catalysts, measured by Hg-porosimetry.

variations were more pronounced. After about 140 h of operation, all catalysts showed stable and similar conversion levels, between 55 and 65%, except for AMAC-128 which was about 70%; after 300 h conversion increased at about 80%, and remained stable for the rest of operation. Overall conversion was unaffected by macropores and carbon black in AMACs (see Fig. 5).

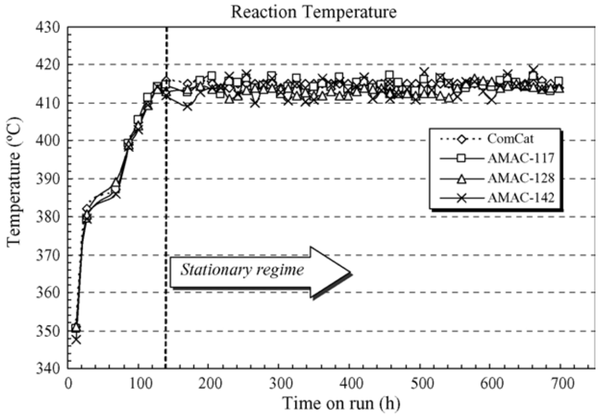

Fig. 3. Reaction-temperature monitoring upon heavy residue hydroconversion using AMAC and ComCat catalysts. Right part of dotted vertical line is stationary regime.

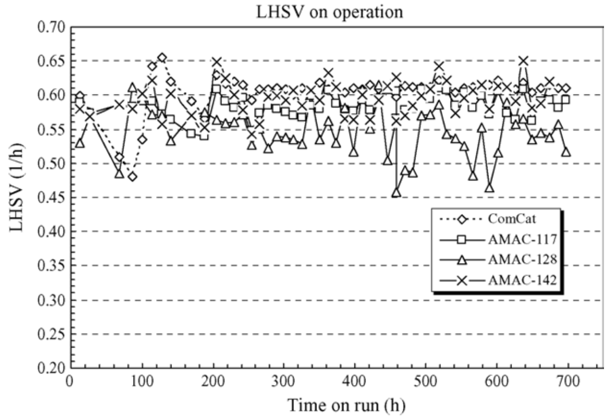

Fig. 4. LHSV variations on the evaluation of AMAC and ComCat catalysts.

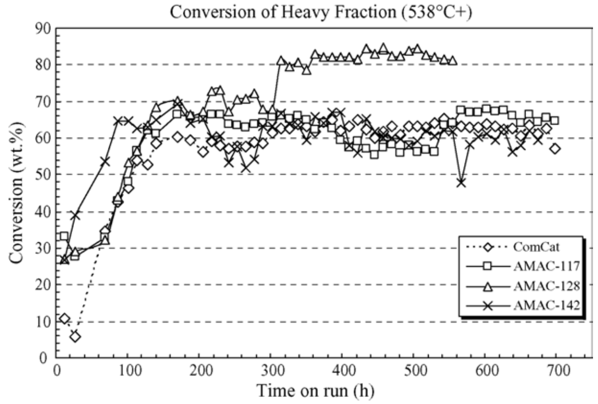

Fig. 5. Conversion of 538 °C+ heavy residue on AMAC and ComCat catalysts.

The level of sulfur removal or hydrodesulfurization (HDS), however, is greatly improved by macropores, as can be observed in Fig. 6. For instance, the sulfur removal deactivation rate drops 46% faster in unimodal AMAC-117 than that in bimodal AMAC-128, -142, and ComCat. Moreover, initial sulfur removal levels of AMAC-128 and -142 are 92 and 89%, respectively, probably ascribed to a combination of macropores and carbon black effects, while ComCat shows 86% HDS. Accordingly, HDS reactions are more favored on NiMo/C in comparison with those on NiMo/Al_2O_3 catalysts [5,6,12].

Hydrodenitrogenation (HDN) was considerably higher in AMAC catalysts in comparison with that in ComCat, particularly in unimodal AMAC-117, as shown in Fig. 7. This result suggests that the removal of nitrogen is more favored in mesopores than in macropores. Moreover, between 500 and 700 h of operation, AMAC-117 (no macropores) and AMAC-128 (smallest macroporous AMAC, macropore peak @1450 Å) showed higher HDN levels than ComCat and AMAC-142, both having average macropore peaks at 3600 and 2692 Å, respectively.

The active phase in the sulfidic NiMo catalyst is usually described as the so-called Type I and Type II ‘‘NiMoS’’ phase. The typical properties of the ‘‘Type I’’ phase are the lower S coordination of Mo and Ni, and the high dispersion of the

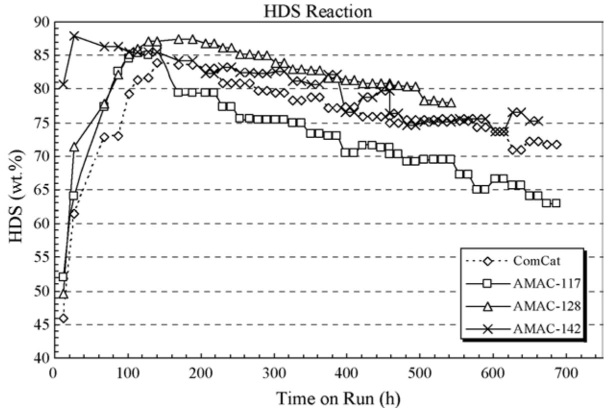

Fig. 6. HDS of 538 °C+ heavy residue on AMAC and ComCat catalysts.

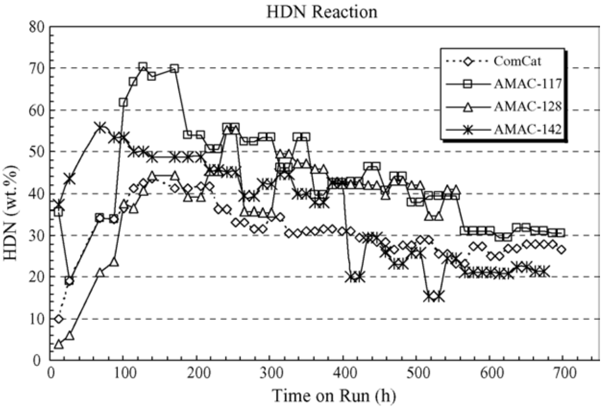

Fig. 7. HDN of 538 °C+ heavy residue on AMAC and ComCat catalysts.

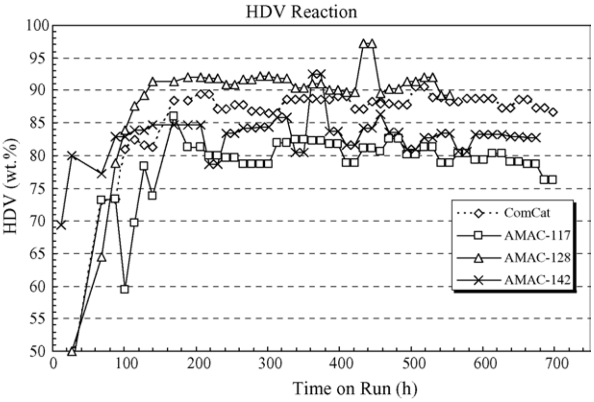

Fig. 9. HDV of 538 °C+ heavy residue on AMAC and ComCat catalysts.

underlying MoS_2, mostly single slabs, having maintained their Mo–O–Al interactions with the support. ‘‘Type II’’ phase has higher intrinsic activity than ‘‘Type I’’ in an HDN reaction [13]. Carbon-supported CoMoS (or NiMoS) structures are more weakly bound to the support than typical alumina-supported CoMoS [14,15]. CoMoS structures found in carbon-supported catalysts had properties much like Type II CoMoS [15,16], in agreement with the observation that support interactions are less important for Type II than for Type I CoMoS [17].

In general, macropores are beneficial in removing heavy metals, such as Ni and V, which are present as porphyrine-like compounds in heavy oils, as can be observed in Figs. 8 and 9. AMAC-catalysts containing macropores were more efficient in hydrodemetallization than the unimodal AMAC-117, clearly indicating the importance of macropores in increasing metals removal levels. Worth mentioning is the case of Vanadium, the most catalyst-deleterious metal. In Fig. 9, HDV levels between 160 and 350 h are approximately 93% in AMAC-128 and 88% in ComCat, though they showed similar HDV levels when deactivation became pronounced. However, AMAC-142, in spite of having macropores at avg. 2690 Å, behaved somewhat lower than AMAC-128.

A tendency to form sediments in AMAC-117, -142, and ComCat is shown in Fig. 10. Formation of total sediments was greatly suppressed in AMAC-117 and -142 in comparison with that in ComCat, especially during the high-activity period (150–300 h), remaining low and stable throughout the test. Presumably, carbon black in AMAC catalysts aids in suppressing Al_2O_3 acidity, which contributes to sediment formation. Notice that when deactivation advances in ComCat, e.g., when coke is deposited on the Al_2O_3 surface, sediments are greatly diminished.

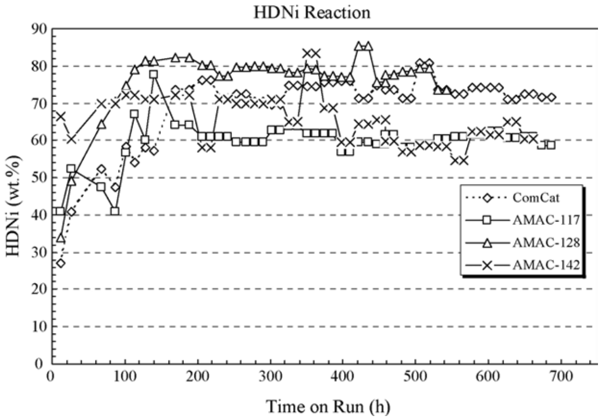

Fig. 8. HDNi of 538 °C+ heavy residue on AMAC and ComCat catalysts.

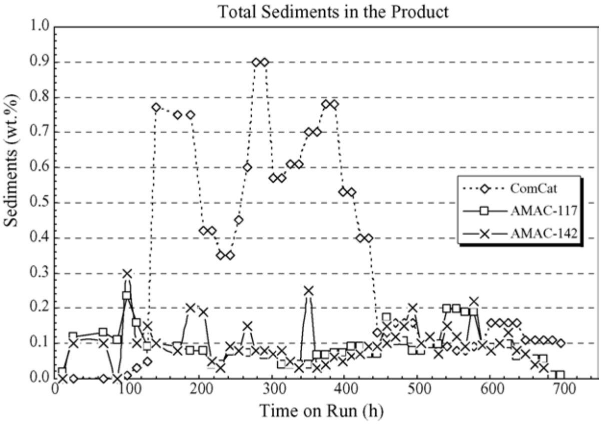

Fig. 10. Evolution of total sediments in the product on AMAC and ComCat catalysts.

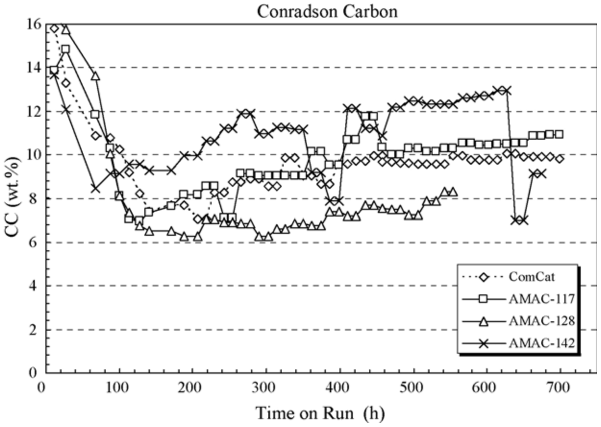

Fig. 11. Evolution of Conradson carbon residue in the product on AMAC and ComCat catalysts.

Table 3
Yields[a] (in wt.%) to indicated oil fraction products using AMAC and ComCat catalyts after 200 h

	Naphta	Kerosine	Diesel	Heavy gasoil	Residue
AMAC-117	4.3	5.9	14.8	43.9	31.3
AMAC-128	5.3	6.2	13.4	43.2	31.3
AMAC-142	5.6	8	16.1	38.1	31.2
ComCat	2	5	13.4	40.2	39.3

[a] From simulated distillation using the ASTM method.

Conradson carbon residue (CCR) is a standard petroleum coking test for characterizing the coke forming tendency of petroleum liquids, and it is an indicator of a catalyst's carbonizing nature when all reaction conditions remain constant, as in the case presented here. The evolution of CCR levels in AMACs and ComCat is shown in Fig. 11, where CCR levels fall rapidly below 130 h of operation because of high activity and a reaction temperature increase (e.g., non-stationary period), while CCR levels are practically stable above 140 h of operation. AMAC-128 showed the lowest levels of CCR formation. AMAC-117 showed similar CCR levels to ComCat, but the former contains carbon black and no macropores. AMAC-142 yielded more CCR than the other AMAC catalysts, probably due to the low carbon black content (see Table 2).

Yields to different hydrocarbon fractions, after 200 h of operation, are presented in Table 3. AMAC catalysts showed a higher tendency to form lighter fractions in comparison with those of ComCat; but a combination of carbon black and larger macropores (i.e., AMAC-142) gave the best results in naphtha, kerosene, and diesel yields.

4. Conclusions

Alumina modified with amorphous carbon black can be a good alternative as a support for H-Oil™ catalysts, especially in decreasing sediment formation. Addition of carbon black to alumina, after almost inert atmosphere pyrolysis, results in shaped strong particles, suitable for high colliding-attrition applications, such as those of ebullated bed reactors. Appropriate mixing and extrusion conditions allow formation of about 22% of total pore volume as macropores. HDS and HDN can be upgraded when combining carbon black and macropores. The presence of carbon black may be promoting a relative abundance of Type II sites in NiMoS species, which are more active than Type I. Macropores are particularly beneficial in removing heavy metals, such as Ni and V, which are present as porphyrine-like compounds in heavy oils; AMAC-catalysts containing macropores were more efficient in hydrodemetallization than AMAC containing no macropores. Yields to valuable light oil fractions, such as naphtha and kerosene, increased using AMAC catalysts.

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