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Carbon modified Y zeolite used as support material for hydroprocessing catalysts

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ABSTRACT

The hydroprocessing activities of Maya heavy crude oil were investigated on NiW catalysts. Two types of supports, carbon modified ultra-stable Y zeolite (AZ) and Y zeolite-carbon (AZC), were prepared. SEM and TEM results show that tungsten phases are well dispersed on carbon modified support whereas these phases are preferentially distributed on part of the carbon covered zeolite support. It is also observed that more stacking of WS_2 slabs are present in zeolite–carbon support and it is due to weak interaction of metal with carbon covered support. HDM and HDS activities increase with increasing percentage of carbon on support and the support having 10 wt% of carbon shows the highest activities. It is also observed that AZ supported catalysts have higher hydrotreating activities compared with the AZC supported NiW catalysts. Deactivation studies show that the presence of carbon into the support may delay deactivation rate during hydrotreating of heavy oil.

1. Introduction

The use of carbon or carbon covered alumina supported catalysts is becoming attractive due to the presence of certain advantages of carbon material. Comparatively, carbon support is of lower cost and can be combusted to recover metals after using in hydroprocessing reactions. Several research reports indicated that carbon supported catalyst is more active than the well-known alumina supported hydrotreating catalysts. Carbon support is inert in nature. Hence when the catalyst is sulfided, all transition metal compounds are expected to convert into the sulfide states. Thus the system may be very simple compared with other supported catalysts in which various types of states were found to be present with sulfide states. It is assumed that since carbon support has very weak adsorption affinity towards hydrocarbon, mainly aromatics and nitrogen compound, it is less prone to poisoning and fouling compared with alumina supported conventional catalyst [1,2]. The poisoning effect of pyridine on thiophene HDS was investigated by Hillerova et al. [2]. It was found that carbon supported catalysts were more resistance during HDS of thiophene in the presence of pyridine than alumina supported catalysts. It was also reported that due to more resistance of nitrogen pyridine poisoning, the HDS activity of thiophene of NiMo/C is three times higher than that of $NiMo/Al_2O_3$ catalyst.

Farag et al. [3,4] studied in detail the HDS activity of carbon and alumina supported catalysts. It was reported that HDS activity of DBT and 4,6 DMDBT of carbon supported catalysts in general is higher than that of alumina supported catalysts. Experimental results during hydrodesulfurization of diesel feed also showed that the carbon supported catalysts have higher activity than alumina based catalyst. Hydrodemetallization activity of Arab heavy atmospheric residue has been studied by Rankel [5]. It is found that carbon supported catalyst showed higher HDM activity than alumina supported catalyst. CoMo/C catalyst has 87% HDM conversion whereas it is around 73 wt% on $CoMo/Al_2O_3$ catalyst. However the CCR removal and HDS conversion are higher on alumina based catalyst compared with carbon based one. It is also reported the activity depends on the type of carbon support.

Maity et al. [6] have conducted HDM and HDS activity studies on carbon modified alumina and carbon–alumina supported hydrotreating catalysts. They reported that when carbon is added to the boehmite and then the added carbon is burnt off, pores having comparatively higher pore diameter are generated. It is also found that the modified alumina has higher HDM and HDS activities compared with carbon–alumina supported catalysts. However, the deactivation on the later case is less.

Hydroprocessing activities over vacuum residue of Maya crude were investigated on carbon supported NiMo catalysts by Salinas et al. [7]. Conversion of the catalysts was not greatly affected by the macropores of carbon; however, it was observed that HDS activity was more favorable on the catalysts which contain more macropores. It was stated that active metal and support interaction of the carbon based catalyst was weak and as a result the formation of more active Type II sites was occurred. High sediment formation was observed for alumina based catalyst compared with the neutral carbon based catalyst. It was also noticed that when the reaction proceeds and carbon coming from the feed was deposited on the alumina surface, the sediment formation decreased. This

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fact indirectly reveals that the presence of carbon indeed suppresses sediment formation. The production of higher percentage of lighter fractions was also observed in carbon supported catalyst.

The use of carbon support for hydrotreating catalyst has various advantages as discussed above. However, the disadvantage of the use of this support is its mechanical strength. For that reason, using carbon with other supports is an alternative. This motivated us to carry out experiments to study the activities of carbon modified zeolite and carbon containing zeolite supported Ni–W catalysts. The catalytic activities are studied with Maya heavy crude hydroprocessing.

2. Experimental

The activities of supported hydroprocessing catalysts are investigated in this work. Two types of supports, carbon modified ultra-stable Y zeolite (USY) and ultra-stable Y zeolite with carbon, have been used to prepare NiW catalysts. Ultra-stable Y zeolite having different amounts of carbon was prepared. The USY zeolite was kneaded vigorously with water solution of acetic acid (1.5 vol%). Boehmite (70 wt%) is used as binder for the catalysts. The required amount of carbon (Aldrich, Darco, # 175KB-G, 60 mesh) was added to the USY and again the mixture was kneaded. The paste was kept overnight and then extruded in the size of 1 mm diameter. The dried extrude was divided into two parts: one part was calcined at 600 °C in air (support designated as AZ-*X*) and another part was calcined in nitrogen atmosphere at 400 °C (support designated as AZC-*X*), where *X* is the percentage of carbon onto the mixture of boehmite and USY. For both cases, the duration of calcinations was 5 h. In this method, from 5 to 25 wt% of carbon was added to the mixture of boehmite and zeolite.

The co-impregnation method was used for the preparation of catalysts having 15 wt% of WO_3, and 5 wt% of NiO. Appropriate amounts of ammonium (meta) tungstate (Fluka), and nickel nitrate (Baker) salts were dissolved into distilled water. The solution was impregnated on dry support and the impregnated samples were allowed overnight at room temperature. Samples were then dried 7 h at 120 °C and calcined at 450 °C for 5 h in flow of air and nitrogen for AZ and AZC supported catalysts, respectively.

The specific BET surface area, pore volume and pore size distribution (PSD) of the catalysts were measured by nitrogen adsorption at 77 K (Quantachrome Nova 2000). X-ray diffractograms were recorded on a SIEMENS D-500 model using a Cu-K_α radiation. The tungsten distribution of Ni-W/AZ-10 and Ni-W/AZC-10 catalysts was measured by a scanning electron microscope (SEM), model XL30 ESEM, Philips.

Transmission electron microscopy (TEM) was performed on a Tecnai G2 F30 S-Twin transmission electron microscope operated at 300 kV. The microscope is equipped with a Schottky-type field emission gun and an S-Twin objective lens (Cs = 1.2 mm; Cc = 1.4 mm; point to point resolution, 0.20 nm). The sulfided catalyst was powered and sonicated in n-heptane. One drop was removed with a micropipette and placed onto a copper grid coated with a sputtered carbon polymer.

The total amounts of metals in the feed and products were measured by atomic absorption (Thermoelectron model Solaar AA). Sulfur was analyzed by X-ray fluorescence (HORIBA model SLFA-2100).

Activity of the catalysts was studied in a batch reactor. 5 g of fresh catalyst was sulfided *ex situ* for each experiment. An atmospheric unit was used for sulfidation. In this unit, hydrogen was passed through a container having CS_2. The saturated mixture of CS_2 and hydrogen passed through the reactor. The sulfiding conditions for the activation of the catalyst were temperature of 400 °C; atmospheric pressure; duration of sulfidation of 3 h; hydrogen flow of 40 mL/min. For the activity study, 200 g of Maya heavy crude was taken into the batch reactor (1 L capacity). The sulfided catalyst was transferred into a basket in nitrogen atmosphere very quickly so that catalyst would not contact with air for a long time. The reactor was tightened properly and checked for leakage. The reactor was then purged two/three times with hydrogen gas so that there was no air left inside the reactor. Heating was started from room temperature to the required temperature at the rate of 3 °C/min. Stirring started when temperature reached the set point (400 °C) and the time was noted as the beginning of the reaction at this point. The experimental conditions of the batch reactor were temperature of 400 °C; total pressure of 100 kg/cm^2; catalyst weight of 5 g; Maya crude of 200 g; duration of reaction of 6 h and stirring rate of 750 rpm. Products were separated from the catalyst after reaction and metals and sulfur contents of the products were analyzed.

A continuous micro-flow reactor was also used to study the activity of NiW/AZC10 catalysts at three different reaction temperatures. In this reactor, oxide catalyst was sulfided *in situ* before actual run was started. 10 mL of oxide catalyst was loaded with equal volume of diluent, carborundum (0.2 mm size). Both catalyst and carborundum were mixed and divided into five parts. Each part of the mixture was loaded into the reactor at a time and with intermittent tapping. The catalyst was then dried for 2 h at atmospheric pressure and 120 °C. After drying, the catalyst was allowed for soaking for 2 h at 150 °C. Light gas oil (LGO) was used for soaking. This light gas oil contains 1.7 wt% sulfur. The actual sulfiding agent was introduced after soaking. The sulfiding agent was light gas oil with dimethyl disulfide (DMDS, 1 wt%). Sulfidation was done at 28 kg/cm^2 pressure at two different temperatures. The first sulfidation was performed at 260 °C for 3 h and finally the catalyst was sulfided at 320 °C for 5 h. Catalytic tests were carried out in a high pressure fixed-bed micro-reactor in up flow mode. The experimental conditions are total pressure of 75 kg/cm^2; reaction temperatures of 380, 390 and 400 °C; liquid hourly space velocity (LHSV) of 1.0 h^{-1}; and hydrogen-to-hydrocarbon ratio of 356 m^3/m^3. Maya heavy oil was used for catalyst activity tests. The first balance was taken after a stabilization period of 9 h.

Boling point distributions of feed and products were determined by thermo gravimetric analysis (TGA). TGA was first calibrated by using the following pure compounds of known boiling point: naphthalene (218 °C), fluorene (294 °C), dibenzothiophene (332 °C), fluoranthene (384 °C), chrysene (448 °C), dibenzo(a)anthracene (518 °C). For an actual case, TGA evaporation temperatures of feed and products were converted to their corresponding normal boiling temperatures from the calibration curve. More details about this experiment have been discussed in our previous work [6].

3. Results and discussion

The specific BET surface area (SSA), total pore volume (TPV), average pore diameter (APD) and pore size distribution (PSD) of carbon modified AZ supports were measured, and the results are given in Table 1. This table shows that the addition of carbon to the zeolite and subsequently burn off the added carbon does not change significantly the pore structure of zeolite. However, in general this process generates pores having higher pore diameters. In a previous work when carbon was added to the boehmite and subsequently burn off the carbon, alumina having higher pore diameter was obtained [6]. Pore size distributions of NiW/AZ-10 and NiW/AZC-10 catalysts are compared in Fig. 1. No drastic difference is observed from this figure. The only noticeable difference is that AZC supported catalyst has more pores in lower pore diameter region and it may be due to the presence of carbon.

Table 1
Physical properties of carbon modified zeolite supports.

Properties	Supports		
	AZ0	AZ10	AZ20
SSA (m^2/g)	267	265	257
TPV (mL/g)	0.71	0.72	0.72
APD (Å)	106	109	112
PSD (vol%)			
1000–500 (Å)	0.18	0.76	1.53
500–200 (Å)	18.92	25.72	17.09
200–100 (Å)	56.52	55.47	46.3
100–50 (Å)	18.01	11.65	20.66
<50 (Å)	6.37	6.4	14.42

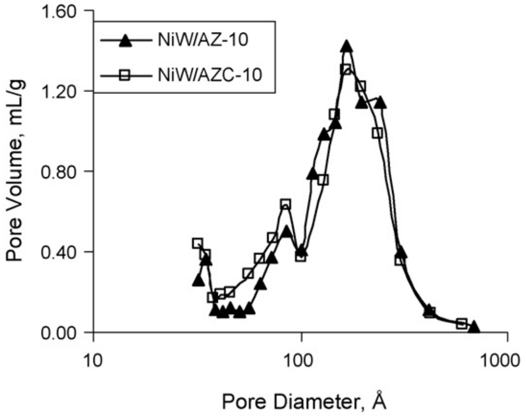

Fig. 1. Pore size distribution of fresh NiW/AZ-10 and NiW/AZC-10 catalysts.

For the same reason, the total surface area of the AZC support is also higher than that of AZ support (SSA of AZ10: 265 m^2/g and SSA of AZC10: 374 m^2/g).

Diffractograms of AZ and AZC supported NiW catalysts are presented in Fig. 2. There are no differences in these two diffractograms. Moreover, due to the overlapping of the spectrums, it is not possible to distinguish the diffractograms for support and active metal. It is only observed that due to the presence of carbon on AZC supported catalyst, the intensity of diffractogram for alumina is reduced.

Scanning electron microscopy has been studied in two (NiW/AZ-10 and NiW/AZC-10) catalysts. The tungsten distribution on these catalysts is shown in Fig. 3. Fig. 3(a) shows that tungsten oxide in NiW/AZ catalyst is eventually distributed through out the catalyst particle. However, the distribution of tungsten oxide in catalyst NiW/AZC (in Fig. 3(b)) is not so even compared with that of catalyst NiW/AZ. In Fig. 3(b) several large black spots (arrows) are observed and these may be bigger molecules of tungsten oxides.

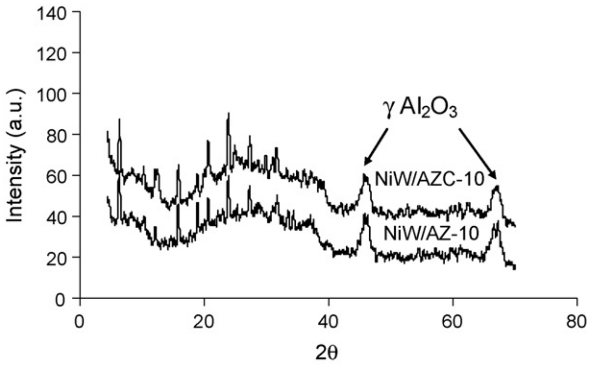

Fig. 2. XRD diffractograms of NiW/AZ 10 and NiW/AZC 10 catalysts.

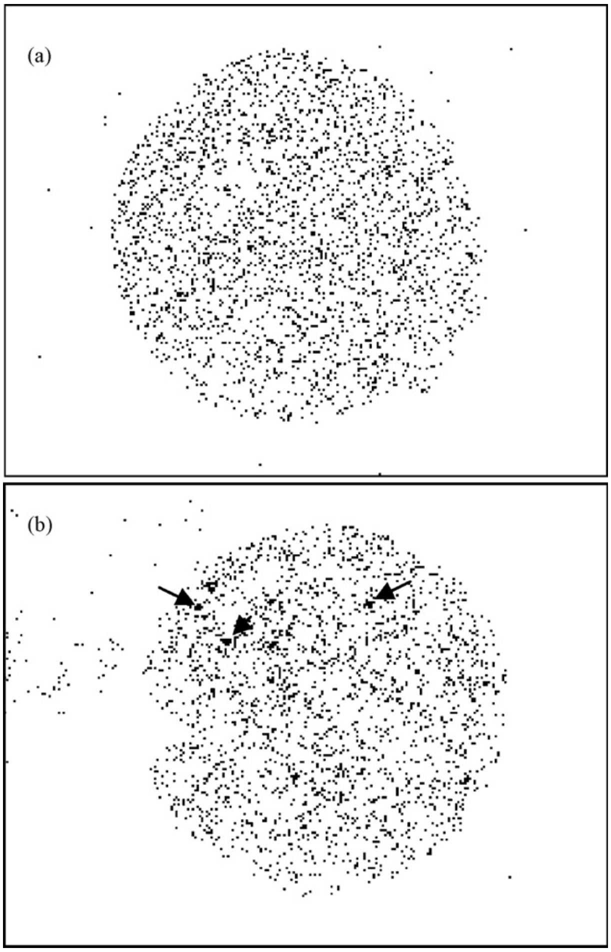

Fig. 3. Tungsten distribution of Ni–W catalysts supported on AZ (a) and AZC (b) (measured by SEM).

Transmission electron microscopy (TEM) of NiW/AZ-10 sulfided catalyst is presented in Fig. 4(a) whereas in Fig. 4(b) and (c) TEM of NiW/AZC sulfided catalyst is given. It is observed from Fig. 4(a) that WS_2 fringes having maximum four slabs are formed. The average size of this (black arrow) is around 4.37 nm. However, most of the WS_2 fringes are bigger in size and it is found around 9 nm (white arrow). Mostly the staging of the WS_2 fringes is two to three. The average staging of these fringes on AZC supported catalyst is higher and it is even nine slabs at maximum (black arrow in Fig. 4(b)). The average slab size on this supported catalyst is around 2.9 nm (Fig. 4(b), black arrow). It is noticed from Fig. 4(c), that at least four WS_2 blocks are together in different orientations. It is also noticed that sulfide fringes are more evenly scattered on the AZ surface (Fig. 4(a)). These fringes are more centered in specific zone of the AZC support. It can be stated that agglomeration of WS_2 phases occurred in the presence of carbon and that is why its number of staging is higher than that for AZ supported catalyst. On the other hand, due to the less interaction between metal and support on AZC, shorter slabs with more stacking metal sulfides are formed. The agglomeration of tungsten oxide phases is also observed from our SEM result.

The hydroprocessing activities of AZ and AZC supported NiW catalysts have been studied in a batch and as well as in a continuous micro-reactor. Properties of Maya heavy crude oil used as feed are given in Table 2. This table shows that Maya crude oil contains high amount of impurities (3.5 wt% sulfur and 322 wppm metals).

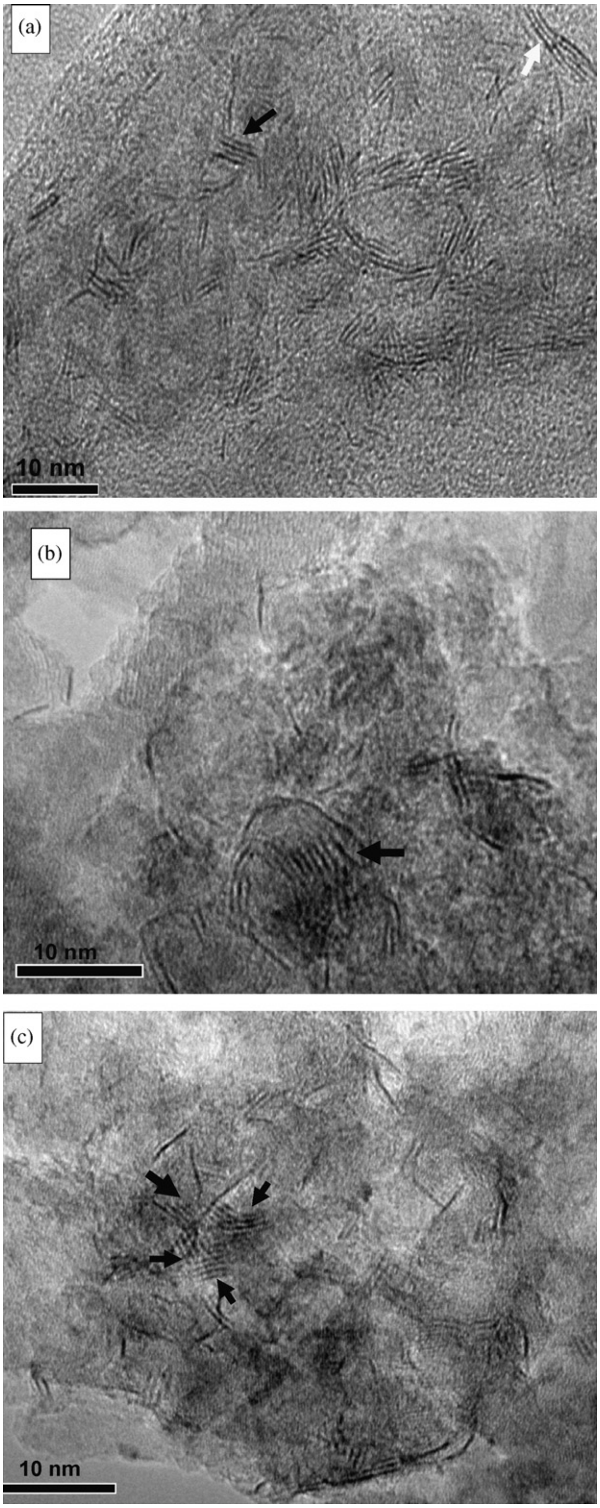

Fig. 4. TEM images of Ni–W catalysts supported on AZ (a) and AZC (b) and (c).

The hydrodemetallization (HDM) and hydrodesulfurization (HDS) activities of AZ and AZC supported catalysts are presented in Figs. 5 and 6, respectively. These activities were studied in a batch reactor at 400 °C. Fig. 5 shows that the HDM and HDS activities slightly increase with increasing percentage of carbon and the maximum activities are obtained on AZ-10 supported catalyst. Further increases of carbon content do not markedly change activities. When we compare carbon modified zeolite and carbon containing zeolite supported NiW catalyst, it is found that AZ supported catalyst has slightly higher activities. From both figures it is noted that HDM activity is higher than HDS activity for all catalysts studied in batch reactor.

Table 2
Properties of Maya heavy crude.

Properties	Values
C (wt%)	86.9
H (wt%)	5.3
N (wt%)	0.3
S (wt%)	3.52
Metals (wppm)	
Ni	49.5
V	273
API gravity	20.99
Ramsbottom carbon (wt%)	11.01
Asphaltenes (in C_7) (wt%)	11.2
Density 20/4 °C	0.9251

The HDM and HDS activities of NiW/AZC-10 catalyst were also investigated in a continuous micro-flow reactor and the results are given in Fig. 7. The conversions of HDM and HDS are measured at three different reaction temperatures 380, 390 and 400 °C. It is noted from this figure that at 380 °C, both HDM and HDS activities decrease with time-on-stream (TOS). This decrease in activity is attributed to the initial period of deactivation due to coke deposition. After this period stable conversion is found at higher reaction temperatures. Even, it is observed that at higher reaction temperature 400 °C, HDM and HDS activities slightly increases with TOS. In other experiments we have also observed that the hydrotreating activities of carbon supported Mo catalysts increase with TOS and it is more prominent when the reaction was studied at higher temperature. Moreover, it is also found that carbon supported catalyst has higher activities than alumina supported one particularly at higher reaction temperature.

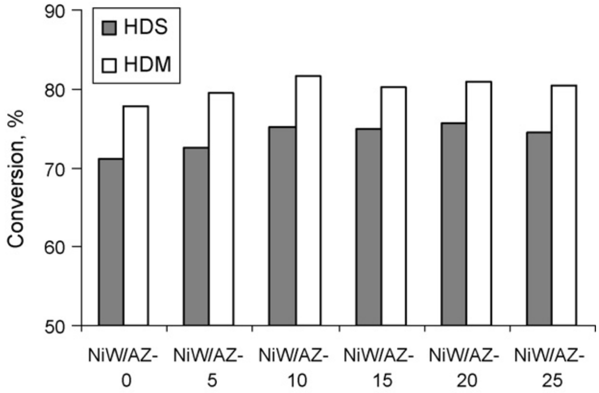

Fig. 5. HDS and HDM of NiW/AZ-*X* catalysts.

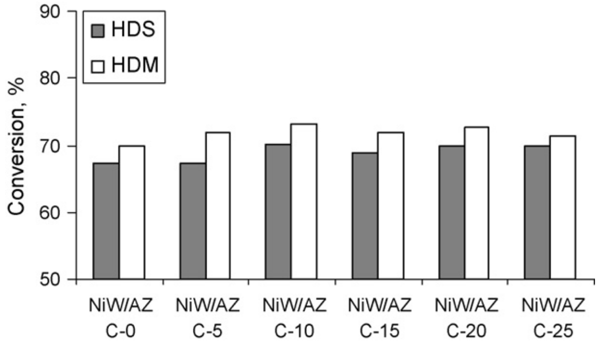

Fig. 6. HDS and HDM of NiW/AZC-*X* catalysts.

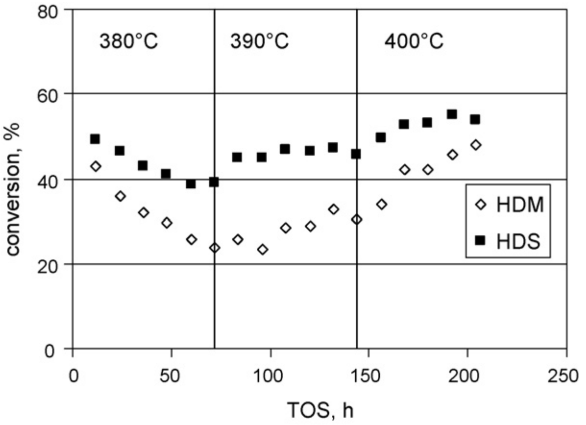

Fig. 7. HDS and HDM of NiW/AZC-10 catalyst in micro-reactor at three different temperatures.

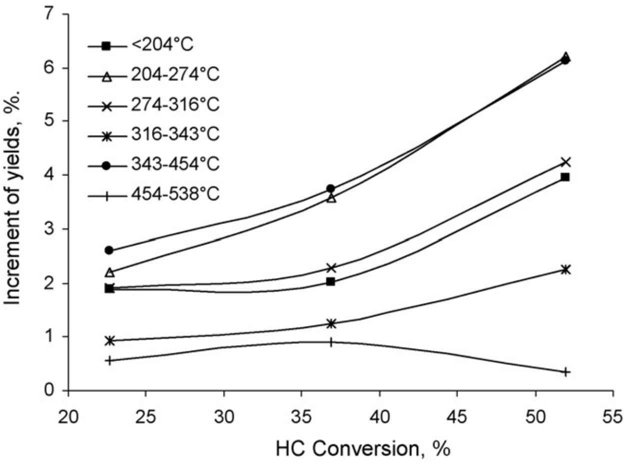

Fig. 8. Hydrocracking selectivity of NiW/AZC-10 catalyst.

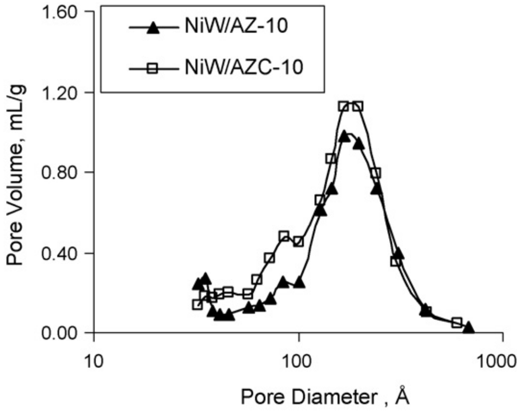

Fig. 9. Pore size distribution of spent NiW/AZ-10 and NiW/AZC-10 catalysts.

The hydrocracking activity (HC) of NiW/AZC-10 catalyst is presented in Fig. 8. The product distributions at different boiling rages were measured by TGA. In this figure increment of composition of lighter fractions in the product with respect to the feed has been plotted against percentage of HC (538 °C+). The heavier fraction particularly residue (538 °C+) is more selectively converted to lighter products of 204–274 °C and 343–448 °C boiling ranges. It is also noticed from this figure that the higher the temperature the higher the HC, and the increase is even higher when reaction temperature increases from 390 °C to 400 °C. When reaction temperature raises from 380 °C to 390 °C, yield of products (438–538 °C) also increases. However, with further increase of reaction temperature, yields in this boiling point region decrease. It indicates that at higher temperature, oil fractions of this boiling point region are converted to more lighters fractions.

Table 3
Hydrocracking activity of AZ and AZC supported NiW catalysts.

	Product distribution (wt%)		
	Feed	NiW/AZ 10	NiW/AZC 10
<177 °C	6.08	17.98	10.53
177–204 °C	4.23	6.85	6.83
204–274 °C	10.62	18.53	19.11
274–316 °C	5.72	9.06	10.04
316–343 °C	3.76	5.32	6.00
343–454 °C	14.99	17.76	20.33
454–538 °C	10.10	8.64	10.38
>538 °C	44.49	15.87	16.77

The hydrocracking activity of AZ-10 and AZC-10 supported NiW catalysts is given in Table 3. The products are obtained from batch reactor at 400 °C reaction temperature. Although there is no remarkable difference of total conversion, NiW/AZ 10 catalyst produces more light products in lower boiling region (<177 °C).

Two different supports (AZ and AZC) are used for this work. In the first one (AZ), different amounts of carbon is added (up to 25 wt%) and then this added carbon is burnt off. And in the second, the added carbon is not burnt off. It remains with zeolite support. It is observed that AZ supported catalysts show higher HDM and HDS activities than AZC supported one. From our SEM and TEM studies we noticed that when zeolite is covered with carbon, active metals tungsten phases may be agglomerated into the bigger crystalline size of tungsten oxide or sulfide. The TEM results show that WS_2 fringes are evenly distributed through out the catalyst surface whereas, these fringes preferentially distributed on some preferable sites. The population of WS_2 slabs is also higher on the AZ supported catalyst. It indicates that tungsten phases on AZ support are more dispersed compared with those of AZC supported NiW catalyst.

Carbon and metals (vanadium and nickel) are deposited into the catalysts pore during hydroprocessing of Maya crude. The changes of physical properties due to these depositions are measured. The spent catalysts obtained after 6 h of operation in the batch reactor were washed by a Soxhlet process. The pore size distributions of two spent catalysts (NiW/AZ-10 and NiW/AZC-10) are presented in Fig. 9. PSD for the same fresh catalysts is compared in Fig. 1. When these two figures are examined, it is noted that the pore structure of AZ supported catalyst is reduced noticeably due to the depositions. The vanadium deposition on these two spent catalysts is also measured. The vanadium deposition on NiW/AZ-10 catalyst is 0.53 wt% whereas it is 0.42 wt% on NiW/AZC-10. These results indicate that the deactivation on carbon covered supported catalyst is lower which is in good agreement with our previous results [6].

4. Conclusions

The hydroprocessing activities of Maya heavy crude were performed on two different supported NiW catalysts. Two types of supports (zeolite modified by carbon and zeolite–carbon) were used for this study. The pore size of the support is not changed by carbon addition. With increasing the percentage of carbon, slight increases of HDM and HDS activities are observed up to 10 wt% carbon. With the addition of further carbon, activities are not changed significantly. Both HDM and HDS conversions are higher on AZ supported catalysts compared with those of AZC supported one. SEM and TEM results show that tungsten phases are well dispersed on carbon modified support whereas these phases are preferentially distributed on part of the carbon covered zeolite support. It is also observed that more stacking of WS_2 slabs is present in zeolite–carbon support, which is result of the weak interaction of metal with carbon covered support. The presence of carbon into the support may delay the rate of deactivation during hydrotreating of heavy oil.

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