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Upgrading of Heavy Crude Oil with W-Zr Catalyst

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Abstract

The main problem of new crude oil reserves is the incipient increase of heavy crude oils in the American continent, *i.e.* USA, Mexico, Canada and Venezuela. These types of crude oils require several treatments before refining. One of these treatments can be hydrocracking. In this petroleum refining process, it is possible to modify the heavy crude oils to light crude oils. In this paper, we try to use hydrocracking to improve the quality of raw heavy crude oil, through some chemical transformations C-H binding rupture using a catalyst containing active metals such as tungsten and zirconium (W-Zr). After the crude oil was hydrocracked in presence of this novel bimetallic catalyst, the hydrocracked products showed lower content of asphaltenes, resins, sulfur and nitrogen. Also positive changes in the viscosity of crude oil measured as a decreasing of this value were observed. The American Petroleum Institute (API) gravity was significantly increased 6 units. Consequently, all these changes confirmed that the upgrading of the heavy crude oil was successful.

Keywords

1. Introduction

The International Energy Agency reported in 2009 that the demand for crude oil has increased over the last 40 years by 150% and, by 20% in the past two decades, to reach a current demand of 80 million barrels per day. It is projected to grow 1.4% per year for the next 30 years and reach 118 million barrels per day by 2030 [1] [2]. This oil demand comes at time when there is a gradual reduction in the supply of relatively cheap conventional

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crude and new discoveries of light field oil do not cover this demand [2] [3]. It is estimated that there are 8 - 9 trillion barrels of heavy crude oil and bitumen around the world, of which potentially 900 billion barrels of crude oil are commercially exploitable with modern technology [3]-[5]. In 2015, the growth of oil sand exploitation will exceed 2 to 3 times than the conventional crude oil production. Moreover, better methods are needed to upgrade partially the heavy crude oil before further processing in refineries in order to convert it into light crude oil [4]-[7].

In the catalytic hydrocracking of heavy crude oil, it is necessary to snap the asphaltenes, because they are extremely large molecules. These molecules consist of highly condensed material, heterocyclic and aromatic rings containing sulfur, nitrogen, oxygen, and metals (mainly vanadium and nickel). Therefore, some of the catalysts for hydrogenation contain nickel, tungsten, molybdenum, cobalt or zirconium [8] [9]. For example, molybdenum, tungsten and nickel are widely used as catalysts in refining processes such as hydrocracking, hydrodesulphurization and hydrodenitrogenation. These catalysts are supported on porous materials like crystalline alumina [10].

Moreover, the acid-base properties of these catalysts may help to increase the yield of gasoline and other light hydrocarbons in crude oil processing and also to produce environmentally friendly products [9]-[14].

The purpose of this work is to study the behavior of an acid catalyst formulated with tungsten and zirconium, in the upgrading of the properties of a heavy crude oil. The study of viscosity decreasing and the changes in structural composition of heavy crude oil after the reaction were analyzed [15]-[17]. The paper also examines the decreasing of asphaltenes, resins, sulfur and nitrogen compounds and the increase of API gravity.

2. Experimental Section

2.1. Preparation of Catalyst

The active elements of this catalyst are zirconium, tungsten and oxygen. 5 grams of $ZrOCl_2 \cdot 8H_2O$ (Aldrich 99%) were dissolved in 300 mL of water using a beaker; the content was stirred at room temperature. A solution of 15 grams of $Na_2WO_4 \cdot 2H_2O$ (FLUKA 98%) in 100 mL of water was also prepared and added to the solution of $ZrOCl_2 \cdot H_2O$. The resulting solution immediately turned turbid. After stirring this solution for about 30 minutes, 200 ml 1 N of HCl (MERICHEM 37%) was also added and the mixture was stirred for one more hour and allowing it to stand still overnight at room temperature. The precipitate formed was separated by filtration.

2.2. Activity Tests

The activity tests were carried out in a Parr batch reactor. During the experiments, 200 g of heavy oil were mixed with 5 g of the W-Zr catalyst. Before each experimental test, the reactor was purged with H_2 and stabilized at the required reaction pressure, temperature and stirring rate. The hydrogen pressure was increased to 10.8 MPa, and the reactor was heated to the reaction temperature of 653 K, at 1000 rpm. Three reaction times were evaluated 30, 45 and 60 minutes, the product samples were recovered at the end of each test. The physical and chemical properties of the products from heavy oil upgrading were characterized in accord to the ASTM methods.

2.3. Characterization

Thermogravimetric analyses (TGA-DTA) were obtained with a Perkin-Elmer 1700. The nature of the acid sites of catalyst was analyzed by Pyridine thermo desorption-FTIR, using a spectrophotometer Nicolet FTIR Magna 560. A quartz cell was used for infrared spectrometry with 4 cm^{-1} of resolution, using KBr as blank. Temperature programmed reduction was carried out in an equipment AMI-200 ZETON-Altamira coupled to thermal conductivity detector (TCD) using a certified gases mixture, 10 vol-% of Hydrogen in Argon from 303 K to 1123 K with heating rate of 10 K/min and recording the changes in sample with thermal conductivity detector. The detector calibration was carried out at 313 K using a 57 uL loop. In order to characterize the metallic sites of this W-Zr liquid phase catalyst, this was supported on inert alumina, dried at 383 K in air static atmosphere during 4 hours before H_2-TPR. Physical and chemical properties of heavy oil and products were characterized. API gravity was measured according ASTM-D-287 method. The viscosity was determined using a rotary viscometer; heavy crude oil was put into a sample cup and kept at 298, 310 and 327 K over 20 min, then measurement was conducted according to ASTM-D445 method. SARA analysis (saturates, aromatics, resins and as-

phaltenes) were determined by ASTM-D-4124 method. Sulfur content in the crude oil was measured by ASTM-D4294 method.

3. Results and Discussion

The catalyst W-Zr was characterized using the solid precursor's mechanical mixture in order to obtain the thermal transformations by TGA and DTA.

3.1. Thermogravimetric Analysis

The DTA and TGA plots of catalyst are shown in **Figure 1** and **Figure 2** respectively. The obtained results showed that the catalyst weight is reduced which depends, in part of the composition of the sample [18] [19].

In a first zone, the catalyst showed changes at temperatures in the range of 298 - 373 K. The weight loss was about 3.6 wt% and it was attributed to the removal of fisisorbed water. These are stable octahedral structures of H_2O molecules that form hydrogen bonds with the acid protons.

In a second stage the weight loss was 33.6 wt% and occurred between 388 and 585 K and corresponded to the removal of crystallization water that leads to the formation of anhydrous species such as Na_2WO_4 and $ZrOCl_2$. These two stages showed different mass loss; both are highly endothermic [20].

The third stage is characterized by the decomposition of the tungstic acid which occurs with great difficulty. A weight loss of 6.2 wt%, between 585 and 613 K, attributed to the destruction of stable bonds in this volatile
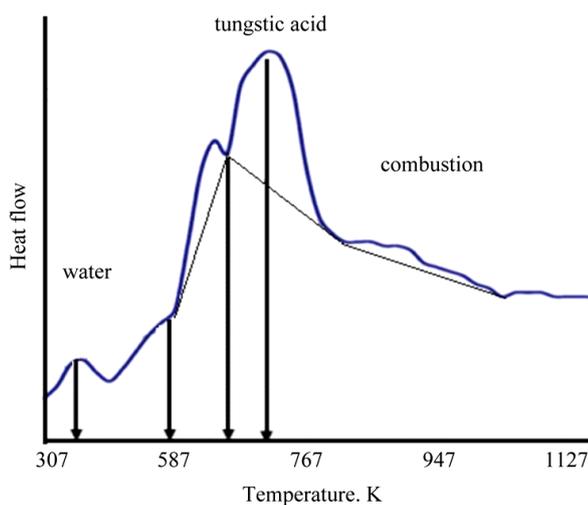
Figure 1. DTA curve for W-Zr catalyst.
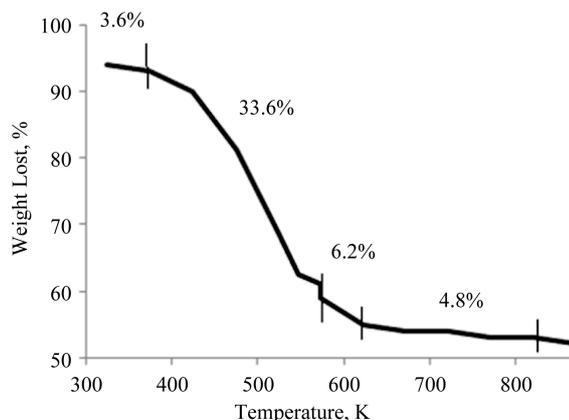
Figure 2. TGA curve for W-Zr catalyst.

compound. The maximum rate of mass loss and DTA curve shifts to a positive zone, above the baseline, which confirmed an exothermic process, see **Table 1**.

The fourth stage was also characterized by small variations in rate and weight loss of 4.8 wt% between 613 and 803 K, which was attributed to the breaking of binding metal-chlorides. All reactions were highly exothermic, during the increment of the temperature in the analysis.

The mass loss was related to the following stages, according to the enthalpy changes observed by DTA: 1) desorption of fisisorbed water before 383 K; 2) at 388 K removal of crystallization water leading to anhydrous species such as Na_2WO_4 and $ZrOCl_2$; 3) decomposition of tungstic acid between 585 and 613 K and 4) oxidation of remaining Cl-Zr and Cl-W species, breaking the bindings of metal-chlorides between 613 and 803 K [21].

3.2. Pyridine Thermo Programmed Desorption (TPD) by FTIR

The IR spectroscopy is widely used to detect adsorbed pyridine and to distinguish different acid sites. FTIR pyridine adsorption spectra at 298 K and the spectra of TPD at 373, 473 and 523 K of W-Zr catalyst were shown in **Figure 3**. The spectra showed a sharp pyridine absorption-desorption bands at 1487, 1539, 1628 and 1643 cm^{-1}. Pyridine molecules bonded to Lewis acid sites absorb at 1604 and 1444 cm^{-1}, whereas those responsible for Brönsted acid sites (pyridinium ion) showed absorbance at 1539 and 1628 cm^{-1} [22]. The band at 1487 cm^{-1} is a combined band originated from pyridine bonds to both Brönsted and Lewis acid sites. **Table 2** shows the Bronsted acid sites, while **Figure 3** shows the FTIR pyridine TPD at different temperatures which could be confirmed elsewhere [23] [24].

Table 1. DTA and TG results for W-Zr catalysts.

Temperature, K	Weight Loss, wt%	Thermal Process
298 - 373	3.6%	Endothermic
388 - 585	33.6%	Exothermic
585 - 613	6.2%	Exothermic
613 - 803	4.8%	Exothermic
TOTAL	48.2%	Highly Exothermic

Table 2. Brönsted acid sites at different temperatures for W-Zr catalyst.

Temperature, K	Brönsted (a.u.)
523	4.923
473	5.180
373	6.628
298	6.458
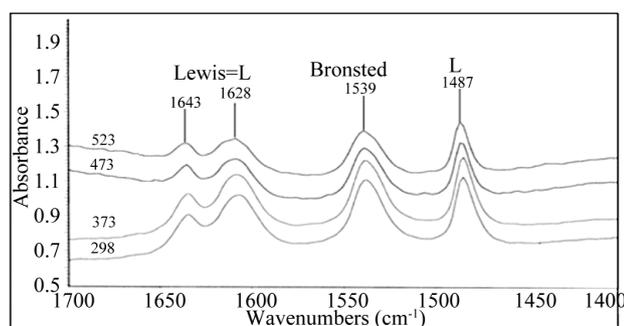
Figure 3. Acid sites distribution using pyridine TPD-FTIR of W-Zr catalyst.

3.3. Temperature Programmed Reduction (H₂-TPR)

The W-Zr catalyst was analyzed by Hydrogen TPR, starting the experiment at 303 K, calibrating at zero the signal of TCD. Two main reduction profiles are shown in **Figure 4**, one first peak observed with a maximum temperature at 837 K attributed to the tetragonal and monoclinic phases of zirconia reduction. And the second peak profile was shown with a maximum reduction temperature of 1039 K attributed to tungsten species reduction of higher hydrogen consumption, with 78.5% of total reduction obtained (see **Table 3**). In accord to these reduction results the active sites of W-Zr catalyst are able to hydrogenate heavy crude oil, considering the reaction temperature is possible that the influence of zirconia can be higher than tungsten in this catalyst.

3.4. Viscosity and API Gravity of Upgrading Products

After the reaction, the API gravity was increased from 12˚ to 16˚ and 18˚, because of hydrocraking of resins and asphaltenes. Consequently, the kinematic viscosity was reduced from 15,416 to 391 cSt at 298 K, because of the production of smaller molecular weight structures. Increasing reaction time from 30 minutes to 45 and 60 minutes improved the reaction products quality and a similar behavior was reported elsewhere [25]. The **Table 4** and **Figure 5** show the API gravity increment, after the hydrocracking.

3.5. Effects on the Composition of the Heavy Crude Oil

SARA analyses (saturates, aromatics, resins and asphaltenes) of the heavy crude oil sample, shows that this sample contains 19, 22.5, 33.5 and 25 wt%, of each group of S, A, R and A respectively. After reaction, it was
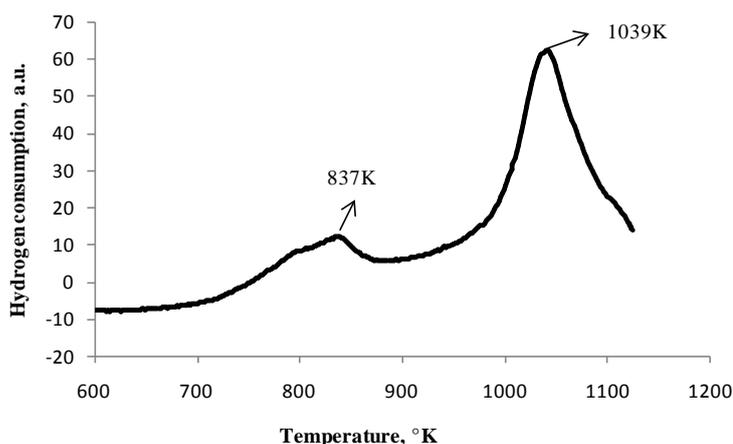
Figure 4. Temperature programmed reduction of the W-Zr catalyst.
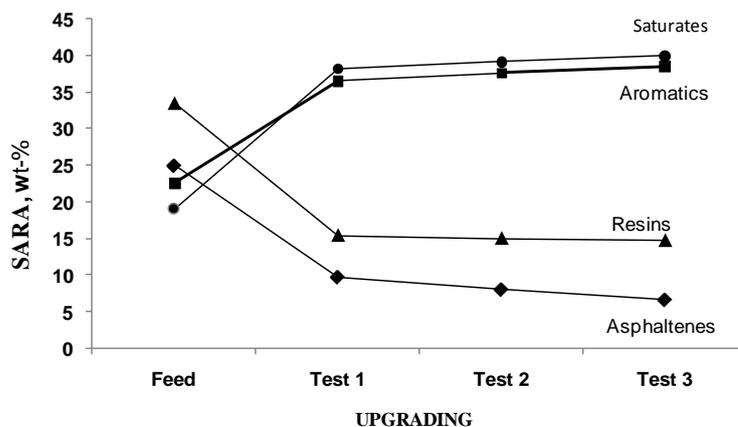
Figure 5. Effect of catalysts W-Zr on the hydrocarbon composition of heavy oil.

Table 3. Physical and chemical properties of the heavy crude oil and the products.

Properties		Heavy crude oil	Test 1 30 minutes	Test 2 45 minutes	Test 3 60 minutes
API		12.5	15.3	16.7	19.0
Viscosity, cSt (K)	@298.0	15,416	391	136	84
	@310.8	9897	278	100	60
	@327.4	5635	185	68	49
Sulfur, wt%		5.13	3.4	3.1	2.8
Nitrogen, wt%		0.78	0.69	0.64	0.62
SARA					
Saturates, wt%		19.0	38.2	39.1	40.0
Aromatics, wt%		22.5	36.5	37.7	38.5
Resins, wt%		33.5	15.5	15.1	14.8
Asphaltenes, wt%		25.0	9.8	8.1	6.7

Table 4. Hydrogen consumption of the reducible species for W-Zr catalyst.

Total	First Peak	Second Peak
Hydrogen consumption	Zirconia reduction	Tungsten reduction
106.00 milimoles H_2	22.75 milimoles H_2 Maximum @837K	83.25 milimoles H_2 Maximum @1039K

observed that there is an increment in the saturated hydrocarbons and aromatic as a result of conversion of resins and asphaltenes, the asphaltenes content was also reduced. These results are in agreement with previous reports [25].

The results obtained indicate several effects of the catalysts in the upgrading of the heavy oil. For example the analysis by families of hydrocarbons reveals that the asphaltene declined, approximately 67 wt% of these were converted to lighter hydrocarbons. On the other hand, the concentration of aromatics was increased from 22.5 in original oil to 36.5, 37.7 and 38.5 wt%, for the reaction times of 30, 45 and 60 minutes, respectively.

3.6. Effects on Content Sulfur and Nitrogen

The catalyst showed a high activity in the removal of sulfur of around 45 wt%. However, sulfur removal also depends on the type of the feed and the operating conditions, which were not severe in the present test. This high catalytic activity can be explained by the total acidity of the catalyst and the hydrocracking properties of the transition metals W and Zr [26]. The sulfur content in the heavy oil was removed up to 3.4, 3.1 and 2.8 wt%, at reaction times of 30, 45 and 60 minutes, respectively. The sulfur removal is caused by the scission of C−S bonds as explained by the removal of thiophenic sulfur using the transition metal salts [27] [28]. These last results showed that the distribution of compounds changed with the increment of reaction time, confirming that this change was due to the conversion of the molecules of resins and asphaltenes.

On the other hand, the content of nitrogen after reaction was reduced from 0.78% wt in the original oil to 0.69 wt% at 30 min, 0.64 wt% at 45 min, and 0.62 wt% at 60 minutes [27] [28]. The nitrogen removal was approximately 20 wt%. **Table 4** summarizes the effect of the catalyst on the nitrogen content.

4. Conclusion

The hydrocracking and hydrogenation capability of the catalyst were responsible for the upgrading of heavy oil. The mild operating conditions in the present test were confirmed by the yields, and higher quality of the up-graded crude oil was obtained. The use of W/Zr catalysts is an interesting alternative for the upgrading of heavy crude oils. These catalysts showed high activity at three different residence times and achieved upgraded products with higher API gravity, lower kinematic viscosity, and lower content of sulfur, resins and asphaltenes.

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