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Gas oil hydrocracking on NiW/USY catalyst: Effect of tungsten and nickel loading

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Abstract

Hydrocraking activity of NiW supported on ultra-stable Y zeolite (USY) with different loading of active component (tungsten) and promoter (nickel) was studied in this investigation. Hydrocracking of petroleum gas oil was carried out in a high-pressure shaking reactor at reaction temperature of 450 °C, contact time of 90 min and catalyst to gas oil ratio of 0.04. A series of NiW/USY catalysts with different nickel (NiO = 0–10.4 wt%) and tungsten (WO_3 = 0–30 wt%) concentrations were prepared using the incipient wetness method. A promoting effect of nickel is observed in all prepared samples and found that the optimum content of nickel was 5 wt%. At this loading of nickel, the values of total conversion and yield of total distillate fuels were 63.3 and 52.3 wt%, respectively. The catalyst activity and properties were enhanced with increasing the tungsten content and the maximum values of total conversion and yield of total distillate fuels were 68.7 and 51.4 wt%, respectively. The catalysts characterizations were presented in terms of SEM, TGA-TPD acidity and TGA thermal stability.

Keywords: Petroleum gas oil; USY-based catalyst; High-pressure shaking reactor

1. Introduction

Hydrocracking process is the most important process in the oil refinery, which breaks up heavier hydrocarbon molecules into lighter hydrocarbon fractions by using heat and catalysts in the presence of hydrogen. Most of the hydrocracking catalysts have three types of easily distinguishable components; these are [1]: active component, promoter and support. The cracking function is provided by supports, where the cracking takes place on strong acid sites in the supports. The most important function of support is maintenance of high surface area for the active component and acidity for hydrocracking reactions. A support material is chosen for given application on the basis of the several important characteristics including its inertness to undesired side reactions, appropriate mechanical properties (attrition resistance, strength, etc.), stability under reaction conditions, a surface area and pore size distribution appropriate for the desired reaction, and its cost [2]. Zeolites are widely used as catalyst support and play an important role in the catalysts used in hydrocracking process because they improve catalytic activity, selectivity, or stability by imparting shape selectivity [3]. Zeolites have been successful because of their crystallinity, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity [4]. Active component and promoter sulphides provide hydrogenation function. The active components responsible for the principal chemical reaction, saturate aromatics in the feed, saturate olefins formed in the cracking, and protect the catalyst from poisoning by the coke. It also produces olefins from paraffins which are much easily activated, i.e., protonated on the acid sites. With addition of the promoter, the strength of Lewis sites and the number of Bronsted sites are increased, and the enhancement in catalytic activity is significant [5]. The role of the promoter is to increase the number of sulphur vacancies and to modify the acid–base properties of the catalyst. The presence of promoter also enhances the production of sulphur anions, thus leading to more numerous of active sites in the reductive atmospheric of the hydrocracking processes. Different active components and promoters were used for hydrocracking process such as molybdenum, tungsten, nickel and cobalt. Mijoin [6] and Breysse et al. [7] concluded that the activity of the promoter catalysts for debenzothiophene transformation is 20 times higher than the activity of the non-promoter catalyst. The use of Co or Ni carbonyls as a precursor was reportedly effective to a preferential formation of Co(Ni)MoS phase [8]. Ali et al. [9]

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reported that NiW-loaded catalysts showed more hydrocracking activity than NiMo catalysts and produced much lighter naphtha. They found that the catalysts loaded with Mo showed lower surface area compared to those having W loadings. The effect of tungsten and nickel content on properties of NiW/USY catalyst as well as on hydrocraking of gas oil has never been investigated so far.

The objective of this work was to convert petroleum gas oil into light products such as LPG, gasoline, kerosene and diesel through hydrocracking over NiW/USY catalyst with different tungsten and nickel content. This paper also presented the effects of tungsten and nickel content on the catalyst properties.

2. Experimental

2.1. Materials

Desulphurized petroleum gas oil (DS-GO) derived from sweet Far-East crude oil with density of 0.8260 kg/l at 15 °C was used in this investigation. This sample was obtained from Shell Refinery Company Bhd., Port Dickson, Malaysia. The high purity gases nitrogen (99.999%) and hydrogen (99.999%) were obtained from Gas Pantai Timur Sdn. Bhd, Malaysia. A mixture of 5% H_2S in H_2 balance was supplied by BOC, UK.

2.2. Catalyst

Commercial USY zeolite with SiO_2/Al_2O_3 mole ratio of 5.5 was obtained from Tosoh USA Incorporation, USA in its Na^+ form. H-USY support was prepared by exchanging the sodium cation (Na^+) in its sodium form zeolite with ammonium ion (NH_4^+) in 4 M NH_4Cl solution and shacked for 24 h. The formed product was consequently filtered and washed with distilled water until chloride free solution was obtained. The sample was kept to dry at 100 °C for 3 h then calcined at 500 °C for 3 h. The chemical composition and physical properties of the USY zeolite provided by supplier are listed in Table 1. Synthesized NiW catalyst with different nickel (NiO = 0–10.4 wt%) and tungsten (WO_3 = 0–30 wt%) concentrations were prepared by impregnation of the USY zeolite with aqueous solution of metal precursor using the incipient wetness method. After impregnation the sample was dried at 110 °C overnight, followed by calcinations at 500 °C for 3 h in a muffle furnace [10,11]. Prior to the reaction tests, the catalyst was pre-treated to increase its performance. About 2 g of the catalyst was placed in a stainless steel tubular reactor of 9 mm inside diameter and 130 mm length placed vertically inside tubular programmable temperature furnace. Nitrogen gas was introduced to the system to purge the air completely out of the system. During this purging operation the programmable temperature furnace was setted to give a heating rate of 10 °C/min. when the temperature of the reactor reached the desired temperature (360 °C), 5% H_2S balance hydrogen gas was allowed to pass through the system at 40 cm^3/min for 3 h. On completion of the run, the furnace was switched off and the gas flow was turned off and allowing the nitrogen gas again to purge the system [12,13].

Table 1
Chemical composition and physical properties of the USY zeolite (Tosoh USA Incorporation, USA)

Zeolite type commodity	USY HSZ-320NAA
SiO_2/Al_2O_3 mole ratio	5.5
Na_2O/Al_2O_3 mole ratio	1.0
X-ray crystallinity (%)	101
Physical state	Solid
Solubility	Insoluble in water
Appearance	White powder

Supplied by manufacture.

2.3. The experimental set-up

The 70-ml stainless steel high-pressure shaking reactor was manufactured with 15.24 cm long and 2.21 cm inside diameter. The reactor was equipped with a vertical tubular furnace of 15 cm length and 5 cm diameter and used as heating source. This furnace was supplied by Watlow, USA, with maximum temperature of 1000 °C. Type K thermocouples were placed outside and inside the reactor wall and were capable of monitoring temperature up to 1100 °C. The schematic diagram of the experimental set-up is shown in Fig. 1.

About 30 g of desulphurized petroleum gas oil (DS-GO) was firstly poured into the reactor, and then the catalyst was added in catalyst to gas oil ratio of 0.04. Hydrogen valve was opened to develop a total hydrogen atmosphere after purging with nitrogen. The reactor was then heated to reaction temperature of 450 °C. The reaction was carried out for a fixed period of time 90 min after the reactor working temperature and pressure were attained. At the end of the run the reactor was cooled down to room temperature and the product was collected for analysis. The reactor was washed with dichloromethane.

The conversion, product yield, and catalyst to gas oil ratio were obtained using the following equations:

$$\%\text{Conversion} = \frac{W_{GO} - W_R}{W_{GO}} \times 100 \qquad (1)$$

where W_{GO}, W_R are weight of gas oil feed and weight of unconverted fraction remained in the liquid product after distillation, respectively.

$$Y_I = \frac{W_I}{W_{GO}} \times 100 \qquad (2)$$

where Y_I is the yield of the product (wt%), I the distillate fraction (gasoline, kerosene, diesel), W_I is weight of the distillate fraction.

$$\text{Catalyst to gas oil ratio} = \frac{W_{CA}}{W_{GO}} \qquad (3)$$

where W_{CA} is weight of catalyst loaded.

2.4. ASTM distillation analysis

ASTM method D 86 was used to determine the product boiling range distribution and to investigate the yield of the lighter products after hydrocracking reaction. The distillation curve of

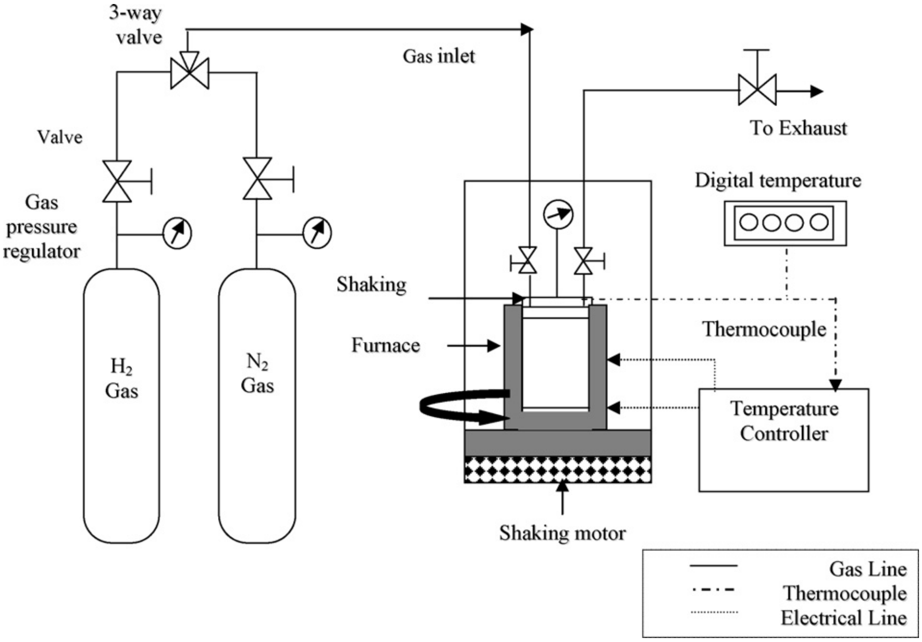

Fig. 1. Schematic diagram of the experimental set-up for hydrocracking of petroleum gas oil.

the liquid products indicates the quantities of useful fractions to the refiner. The ASTM distillation unit was supplied by Hotech Instruments Corp. About 25 ml of sample was poured into the distillation flask. The heater was started and the temperature at the neck of the distillation flask was recorder when the first drop of condensate was collected. The volume of condensate was taken down at the temperature 160, 200 and 240 °C [14,15].

2.5. Gas chromatograph (GC)

The gaseous products were analyzed using a gas chromatograph (Hewlett Packard, model No. 5890 series II) equipped with Porapak Q, 270 cm-length × 3.15 mm stainless steel column (Supelco). The GC was equipped with flame ionization detector (FID). The flame ionization detector (FID) was used to find out the hydrocarbons components presented in gaseous product. The gases detected were hydrocarbons C_1–C_5. The identity of resulting GC peaks was defined by injecting standard gases to FID detector.

2.6. Thermogravimetric analyzer (TGA)

Thermogravimetric analyzer (TGA) supplied by Perkin-Elemer, USA was used to study the thermal stability of the catalysts. About 5 mg of sample were loaded into a platinum pan and heated under nitrogen gas stream of 20 cm^3/min from ambient temperature to 900 °C with a control heating rate of 20 °C/min.

TGA-TPD (temperature-programmed desorption) was conducted on the same TGA instruments using isopopylamine as a base [16,17]. About 5 mg of the sample was placed in a platinum pan and heated under nitrogen gas stream of 20 cm^3/min from ambient temperature to 500 °C with a control heating rate of 20 °C/min and hold at this temperature for 30 min. Then the temperature was lowered to 100 °C followed by injecting isopopylamine for 10 min. The desorption of physosorbed base molecules was allowed to continue at 100 °C for about one hour (until the mass nearly constant). The sample was heated to 700 °C at 20 °C/min to desorb the chemisorbed isopropylamine. The chemisorption curve reveals the density and acid strength of the catalyst sample. The acidity was calculated by the following formula and reported in units of millimoles of acid sites per gram of catalyst:

$$\text{Acidity} = \frac{W(1/\text{Mb})(1000\,\text{mg}/1\,\text{g})}{W_\text{z}} \quad (4)$$

where W is the mass loss due to the desorption of base in the temperature of interest (g), W_z the mass of zeolite-based catalyst after pre-treatment (g), and Mb is the molecular weight of base (isopropyl amine).

TGA was also used to detect the percentages and type of coke deposited on catalysts after hydrocracking reactions. About 5 mg of coked catalyst were loaded into a platinum pan and heated under nitrogen gas stream of 20 cm^3/min from ambient temperature to 110 °C with a control heating rate of 20 °C/min. The nitrogen gas was replaced by the oxygen and temperature was increased to 800 °C.

2.7. Scanning electron microscopy (SEM)

SEM studies were performed using Leica Cambridge Stereoscan 360, UK and Polaron for the coating system (sputter coating). Before the scanning, the powder samples were spread onto the double-side carbon tape, and coated with gold (20–30 nm thickness) in order to increase the conductivity and therefore the quality of the results.

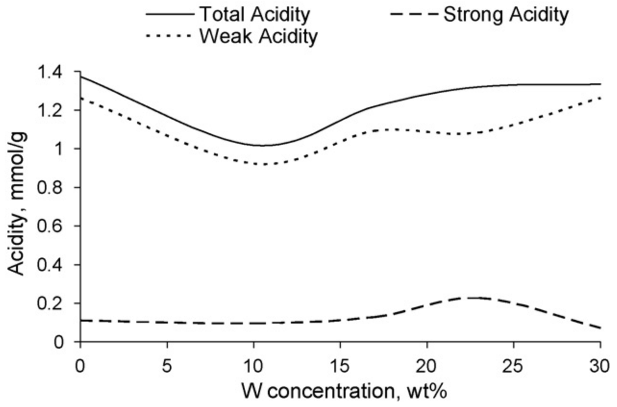

Fig. 2. TGA-TPD acidity vs. tungsten content.

3. Results and discussion

3.1. TGA-TPD acidity measurements

The amounts of weak, strong and total acidity of NiW/USY catalyst with different tungsten and nickel loading obtained by TGA-TPD are presented in Figs. 2 and 3. The acid sites of NiW/USY catalyst were much more significant on all USY-based catalysts. The catalyst acidity became stronger when metal was inserted. The mechanism of acid formation could be due to the metals interact with the zeolite acid sites and induce stronger acidity and the metals themselves provide stronger acid sites. The TPD experiments show that the total acidity (Lewis and Bronsted types) of NiW/USY catalyst was higher at tungsten and nickel content of 23 and 5 wt%, respectively, and therefore showed higher cracking activity than other catalysts.

TGA was also used to carry out the stability of the catalysts. Figs. 4 and 5 show the weight loss (TG) curves of NiW/USY catalyst with different tungsten and nickel concentrations, respectively. It can be seen clearly that all catalysts showed high thermal stability in the temperature up to 700 °C. This stability of the catalysts is favourable to prevent thermal decomposition of the catalysts during the reactions and regeneration process.

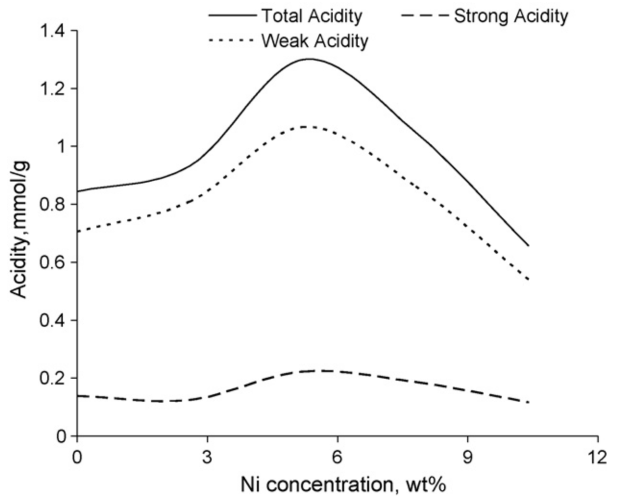

Fig. 3. TGA-TPD acidity vs. nickel content.

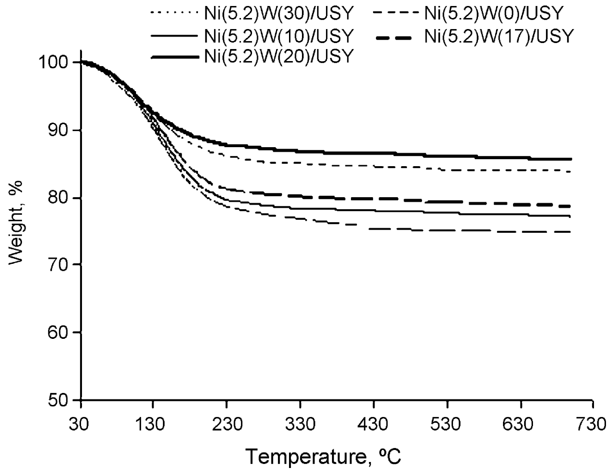

Fig. 4. TGA thermal stability results for NiW/USY catalyst with different tungsten loading.

3.2. Scanning electron microscopy (SEM)

Scanning electron micrographs of USY zeolite and NiW/USY catalyst are presented in Figs. 6 and 7, respectively. SEM images revealed quite regular shaped and sized of USY and NiW/USY particles, and also showed the rougher surface of the USY zeolite and the NiW metals appear to be primarily randomly distributed on the USY surface.

3.3. Coke analysis

The coke content of the catalysts with different tungsten and nickel loading was determined by combustion in a thermogravimeric analyzer and presented in Figs. 8 and 9. For all catalysts used in this study, it can be observed that there are two types of coke formed in two temperature ranges, the weight loss between 150 and 250 °C contributed to soft coke and between 400 and

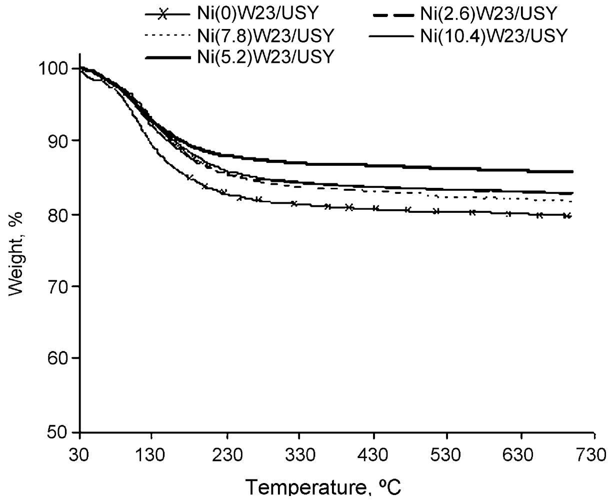

Fig. 5. TGA thermal stability results for NiW/USY catalyst with different nickel loading.

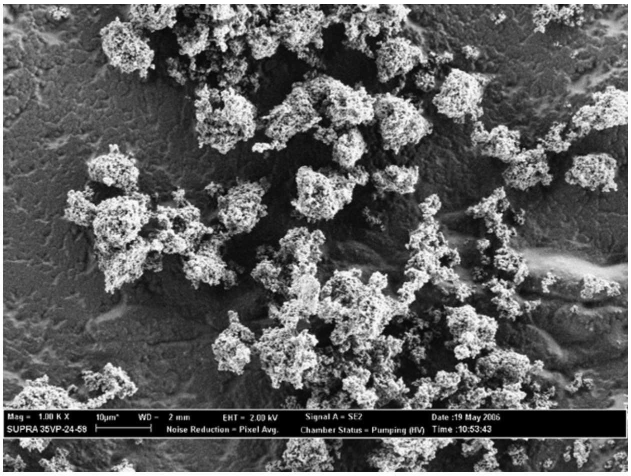

Fig. 6. Scanning electron micrographs of USY zeolite.

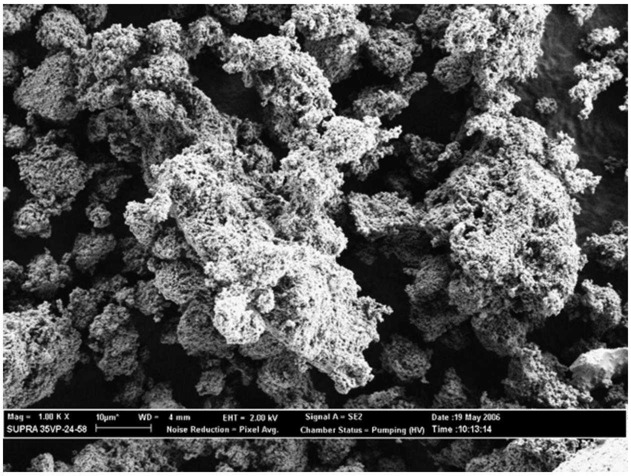

Fig. 7. Scanning electron micrographs of NiW/USY catalyst.

550 °C to hard coke. The soft coke is preferentially formed on weak acid sites [18] while, the hard coke built up on strong acid sites [19]. Around 5 wt% of coke was formed at low temperature which corresponds to the soft coke, whereas around 15 wt% of coke was formed at high temperature which corresponds to the hard coke.

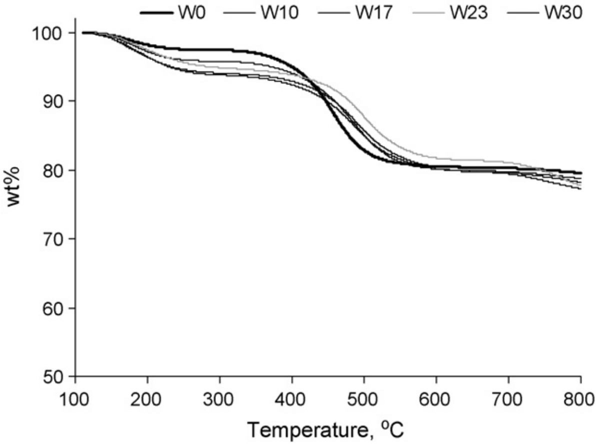

Fig. 8. Profiles of weight loss with temperature of NiW/USY coked catalyst with different tungsten loading.

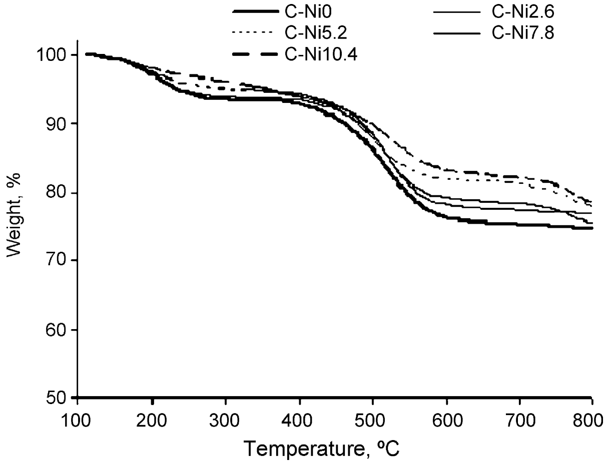

Fig. 9. Profiles of weight loss with temperature of NiW/USY coked catalyst with different nickel loading.

3.4. Product distributions

Prior to carrying out the hydrocracking reaction, it was necessary to establish the mixing characteristic of the reactor. For this purpose, the reaction of hydrocracking of gas oil was carried out and similar run was conducted using the Parr reactor, which considered as perfectly mixed reactor. The results showed that the same results were obtained using both commercial and shaking reactor at the same operating conditions. This confirms that the configuration of new reactor ($L/D = 6$) provides an excellent mixing.

The analyses of the gas oil feed are given in Tables 2 and 3. The hydrocracking activity of the catalysts was measured at reaction temperature of 450 °C, contact time of 90 min and catalyst to gas oil ratio of 0.04 using NiW/USY with different nickel and tungsten concentrations. Table 4 presents the effect of tungsten concentration on conversion of gas oil at a constant nickel content of 5 wt%. For tungsten content less than 17 wt%, the total conversion and yields of all distilled products remained constant and other products (coke and gas) did not change. At low

Table 2
Distillation analysis of the gas oil

Temperature (°C)	Volume (%)
240	IBP
253	5
256	10
263	20
267	30
273	40
279	50
286	60
294	70
306	80
323	90
334	95
346	FBP

Table 3
Elemental composition analysis, wt% of the gas oil

C	85.17
H	14.74
N	0.087
S	0.003
H/C atomic ratio	2.077

tungsten concentration, the catalyst properties are not improved enough to enhance the hydrocracking and hydrogenation reactions, therefore, the total conversion and yield of products were low. The activity of the catalyst is clearly improved upon increasing tungsten concentration. The catalyst activity was increased with increasing the tungsten content and the maximum values of total conversion and yield of total distillate fuels were 68.7 and 51.4 wt%, respectively. At high amount loading of active component, the acid properties of the catalysts were enhanced and hydrogenation sites increased due to a complete occupation of the edges of WS_2 slabs by the promoter, therefore, the increment of hydrocracking activity of the catalysts was observed when the tungsten content reached 23 wt%.

Table 5 shows a total conversion of gas oil and distilled products distribution as a function of nickel content at a constant tungsten concentration of 23 wt%. All nickel containing catalysts manifest higher activity compared to the nickel free catalyst. A total conversion and yield of distilled products were increased with nickel concentration until 5 wt%, and maximum values of total conversion, yield of total distillate fuels, gasoline, kerosene, diesel gas and coke were 63.3, 52.3, 11.5, 5.1, 35.7, 5.2 and 5.8 wt%, respectively. Theses values were obtained at nickel content of 5 wt%, which the promoting effect of nickel is most strongly expressed at this concentration. It is tempting to explain the catalysts activity in terms of dispersion of the active component and promoter. Indeed, at a high nickel concentration, the activity should have been rather low because of the presence of a large amount of NiW and the rather poor dispersion. These results are in good agreement with that obtained by Halachev et al. [20].

Table 4
Gas oil hydrocraking over NiW/USY with different tungsten loading

Tungsten loading (%)	0	10	17	23	30
Conversion	55.1	57.4	56.1	63.3	68.7
Total distilled fuels	41.2	43.3	42.8	52.3	51.4
Gasoline	11.4	10.7	9.2	11.5	10.7
Kerosene	9.1	9.1	8.6	5.1	10.7
Diesel	20.7	23.5	25.0	35.7	30.0
Gas yield	8.4	8.8	8.1	5.2	10.5
Gas composition (mol%)					
CH_4	0.0	0.0	0.1	0.0	0.0
C_2H_4	0.2	0.2	0.2	0.3	0.2
C_2H_6	45.8	37.8	37.9	42.4	50.6
C_3H_6	1.2	1.4	1.4	1.9	1.2
C_3H_8	28.6	35.2	31.8	29.2	29.4
C_4H_{10}	16.9	22.8	20.2	18.3	16.7
$C_5{=}$	7.3	2.6	8.4	7.9	1.9
Coke yield	5.5	5.3	5.2	5.8	6.8

Table 5
Gas oil hydrocraking over NiW/USY with different nickel loading

Nickel loading (%)	0	2.6	5.2	7.8	10.4
Conversion	49.8	52.3	63.3	52.0	54.8
Total distilled fuels	37.0	40.8	52.3	37.8	39.5
Gasoline	9.1	10.6	11.5	10.6	11.4
Kerosene	7.7	9.9	5.1	10.3	6.5
Diesel	20.2	20.3	35.7	16.9	21.6
Gas yield	7.8	7.1	5.2	8.8	10.1
Gas composition (mol%)					
CH_4	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.3	0.2	0.3	0.1	0.0
C_2H_6	37.5	38.3	42.4	52.1	30.2
C_3H_6	2.3	1.6	1.9	1.1	0.0
C_3H_8	33.8	35.0	29.2	29.3	34.1
C_4H_{10}	26.1	24.9	18.3	17.4	35.7
$C_5{=}$	0.0	0.0	7.9	0.0	0.0
Coke yield	4.0	4.4	5.8	5.4	5.2

4. Conclusions

In the present study, hydrocracking reaction of petroleum gas oil in a high-pressure shaking reactor was investigated using a series of NiW/USY catalysts with different nickel (NiO = 0–10.4 wt%) and tungsten (WO_3 = 0–30 wt%) concentrations. From the results, the following conclusions are obtained. The catalyst activity and properties were enhanced with increasing the tungsten and nickel content. It was found that the optimum contents of tungsten and nickel were 23 and 5 wt%, respectively. As a result, the total conversion and yield of distillate products reached the maximum point at this loading of tungsten and nickel. This is in a good agreement with characterization results of catalysts. As evidenced by characterizations of catalysts all catalyst possessed higher acidity with good balance between strong and weak acid sites and also showed very good thermal stability.

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