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Development of Zeolites-based Catalysts for Hydrocracking of Gas Oil

by

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Final Report

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Appendix A

Technical Report

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Abstract

In this project, USY zeolite supported NiMo, CoMo, NiW and CoW were prepared using the incipient wetness method. Over NiW/USY catalyst, the total conversion and distillate fuels were 15.54 and 15.77 wt%, respectively higher than those obtained over unloaded USY zeolite. Then NiW/USY catalyst with different nickel and tungsten loadings were prepared. It was observed that at tungsten and nickel loadings of 23 and 5 wt%, the total conversion and yield of total distillate fuels were 63.35 and 52.35 wt%, respectively. A series of NiW supported on mesoporous MCM-48 with different SiO_2/Al_2O_3 ratios was prepared to study the effect of alumina on the acidic properties of synthesized catalysts. MCM-48-USY composite materials were also prepared by coating USY zeolite by a layer of MCM-48 mesoporous material at different SiO_2/USY ratios and used as support for nickel and tungsten catalysts. The maximum values of total conversion and distillate fuels were obtained at SiO_2/USY ratio of 0.5. It was found that the optimum operating conditions for hydrocracking of gas oil over prepared NiW/MCM-48 catalyst are: reaction temperature of 465 °C, contact time of 30 min and catalyst to gas oil ratio of 0.05.

Keywords: Hydrocracking; Gas oil; Zeolite; Modeling; High-pressure reactor

1. Introduction

The conversion of heavy petroleum fraction into valuable products has been achieved mainly by thermal cracking, catalytic cracking and hydrocracking (Yang et al., 1998). In thermal cracking process, hydrocarbons with higher molecular weight in heavy oils can be transformed to lighter hydrocarbon products by thermolysis at a higher temperature, which is accompanied with the formation of coke. The development of thermal cracking process for producing middle distillates has been limited because large amounts of gas and naphtha with lower quality are produced due to over cracking. Catalytic cracking is different from thermal cracking because carbon-carbon bond cleavage of hydrocarbons in the former occurs on a solid acid catalyst. However, the absence of a high partial pressure of hydrogen in the catalytic cracking process not only makes possible the rapid build up of coke on the catalyst but also results in products containing a significant amount of olefinic and aromatic compounds.

Hydrocracking process using a metal supported solid acid catalyst is considered to be a fine method for producing high quality motor fuels. Hydrocracking reactions proceed through a bifunctional mechanism. A bifunctional mechanism is one that requires two distinct types of catalytic sites to catalyze separate steps in the reaction sequence. These two functions are the acid function, which provide for the cracking and isomerization and the metal function, which provide for the olefin formation and hydrogenation (Yang et al., 1998).

Many catalysts used for the hydrocracking process are formed by composting various transition metals with the solid support such as alumina, silica, alumina-silica, magnesia and zeolites. Most of the conventional hydrocracking catalysts are dual functional catalysts. They have a hydrogenation–dehydrogenation function as well as an acidic function. The cracking activity is controlled mainly by the support that is acidic in nature, whereas the hydrogenation–dehydrogenation catalyst activity is due to the metals loaded on the support. High acidity tends to cause coking, which leads to deactivation. In order to prepare a suitable hydrocracking catalyst, a good balance between the two functions has to be maintained.

Zeolites and related crystalline molecular sieves are widely used as catalysts in the industry since they possess catalytically active sites as well as uniformly sized and shaped micropores that allow for their use as shaped selective catalysts in oil refining, petrochemistry and organic synthesis. However, due to the pore size constraints, the unique catalytic properties of zeolites are limited to reactant molecules having kinetic diameters below 10 Å (Maesen et al., 2004). Zeolites have been successful because of their crystallinity, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity (Weitkamp, 2000).

Recently, a group of researchers at Mobil Oil Company reported a series of mesoporous molecular sieves, named M41S materials. These molecular sieves with mesopore diameters of 15-100 Å overcome the limitation of microporous zeolites and allow the diffusion of larger molecules. The most popular members of this family are MCM-41 and MCM-48. Compared to the more familiar MCM-41, MCM-48 provides easier access to guest molecules due to its 3-dimensional pore network. This decreases diffusion limitations and make MCM-48 more resistant to pore blocking (Sun and Coppens, 2002). MCM-48 contains uniform mesopores, which are larger than nanopores and smaller than macropores, which makes the material particularly suited to reactionsinvolving large molecules, such as gas oil. Despite this advantage over MCM-

41, the synthesis of high quality MCM-48 with controlled pore size is more challenging. The synthesis of aluminium containing mesoporous MCM-48 with improved acidic characteristics is important in many catalytic applications. To improve the acidic characteristics of MCM-48, the alumina content (SiO_2/Al_2O_3 ratio) incorporated into framework was investigated in this work. While increasing alumina content increases the activity of the catalyst, the lack of order resulting from silicate substitutions causes structure thermal instability. It is therefore important to optimize the SiO_2/Al_2O_3 ratio to achieve a reactive and stable catalyst.

The selection of a proper catalyst for a given high activity is a complex problem. While microporous zeolites such as Y, ZSM-5 and β are playing important roles in modern petrochemical industry for their abundant uniform microporous structures and strong intrinsic acidities, much attention is being given to the development of mesoporous zeolites that provide larger pores (>2 nm) to allow the conversion of large molecules and thus overcome the limitations of microporous zeolites. At present, a popular resolvent is to prepare a composite zeolites material comprising of both the microporous zeolites matrix and mesoporous material by multi-step crystallization. However, all of these methods mainly aim at modifying mesoporous material on its structure stability and acidity, which are still far away from microporous zeolites (Chen *et al.,* 2006). Despite the intensive research on synthesis, characterization and application of MCM-41 materials, MCM-48, being the cubic member of the M41S family, has received much less attention especially in the field of catalysis. A contraction of the unit cell occurred by substituting the silicon with larger aluminum atoms. The mesoporous molecular sieves MCM-48 possesses bi-continuous and three dimensional pore channels. Consequently, both the diffusional limitation and the pore blockage are reduced as compared to MCM-41. These characteristic properties show its potential applications in catalysis, adsorption and separation (Chang and Ko, 2004). The main objectives of this study are: (1) To synthesize a series of transition metals (NiMo, NiW, CoMo and CoW) supported on USY/MCM-48 supports. (2) To characterize the catalysts in terms of surface area, pore volume, pore size distribution, thermal stability, acidity strength and morphology and (3) To study the performance of prepared catalysts for hydrocracking of desulphurized petroleum gas oil (DS-GO).

2. Materials and methods

2.1 Sample of petroleum gas oil

Desulphurized petroleum gas oil (DS-GO) derived from sweet Far-East crude oil with density of 0.8260 kg/l at 15 ^{o}C was used in this investigation. This sample was obtained from Shell Refinery Company Bhd., Port Dickson, Malaysia.

2.2. Chemicals

The chemicals and reagents used in this present work are listed in Table 1.

2.3. Gases

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.

2.4 Catalysts

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. Commercial $NiMo/Al_2O_3$ catalyst was used as cracking catalyst in preliminary study and was provided by Sud-Chemie AG Germany.

Table 1: List of chemicals and reagents

Chemical/Reagent	Assay	Supplier	Purpose of use
Cetyltrimethylamonium bromide (CTMAB)	99 %	MESB Chemicals	Surfactant template
Sodium hydroxide, NaOH	99 %	Sigma-Aldrich	Precursor
Tetraethyl ortosilicate, (TEOS), $C_8H_{20}O_4Si$	98%	Sigma-Aldrich	Silica source
Aluminium nitrate, $Al(NO_3)_3.9H_2O$	98.5%	AnalaR BDH	Aluminium source
Hydrochloric acid, HCl	37 %	Mallinckrodt	Precursor
N-hexadecyltrimethylammonium bromide (HDTMAB)	99 %	Sigma-Aldrich	Surfactant template
Ethanol, C_2H_5OH	95 %	MESB Chemicals	Solvent
Ammonia, NH_3	28 %	MESB Chemicals	Solvent
Aluminium isopropoxide, $C_9H_{21}Al_2O_3$	97 %	Fluka	Aluminium source
Nickel nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$	98 %	Fluka	Catalyst modification
Cobalt nitrate hexahydrate, $Co(NO_3)_2.6H_2O$	98 %	Fluka	Catalyst modification
Ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$	81.4% MoO_3	Baker	Catalyst modification
Ammonium (meta) tungstate hydrate, $(NH_4)_6 (W_{12}O_{40}).\ H_2O$	85 % WO_3	Fluka	Catalyst modification
Dichloromethane, CH_2Cl_2	100 %	Mallinckrodt	Solvent
Isopropyl amine, C_3H_9N	99.5 %	Fluka	Acidity measurement
Hexane, C_6H_{12}	99 %	Sigma-Aldrich	Solvent

2.5 Analysis system

Different analyses were carried out to determine the composition of feed and products of reaction and to characterize catalysts such as elemental analysis, ASTM distillation analysis and gas chromatograph (GC).

3.6 Characterization of catalysts

The techniques used to characterize the catalysts include: Nitrogen adsorption, Scanning electron microscopy (SEM), X-Ray diffraction, Transmission electron microscopy (TEM) and Thermogravimetric analyzer (TGA).

2.7. Catalyst preparation methods

2.7.1 Preparation of H-USY support

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 in an oven at 105 °C for 3 h then calcined at 500 °C for 3 h.

2.7.2 Mesoporous molecular sieve MCM-48 preparation

The synthesis of high quality mesoporous aluminosilicate material with three Dimensional pore network MCM-48 was undertaken by the conventional hydrothermal pathway similar to the procedure reported by Sun and Coppens, (2002) and Oye et al., (2001) with some modifications. Figure 3.5 shows the block diagram of the preparation procedure of MCM-48. 7.39g of cetyltrimethylamonium bromide (CTMAB) was dissolved in 87.84g distilled water and 1.21g NaOH was added. 10.63g of tetraethyl ortosilicate (TEOS) was subsequently added at room temperature. After 5 min of stirring, different amounts of aluminium nitrate (to give SiO_2/Al_2O_3 molar ratio in the range of 5-125) were added. The mixture was stirred vigorously for 1 h using a magnetic stirrer. The molar composition of gel was 1.0 CTAMB: 2.5 TEOS: 1.5 NaOH: 244 H_2O. The gel formed was transferred into the Teflon bottle supplied by Nalge Nunc International Corporation, USA, and aged for 72 h at 100 °C. Then the sample was quenched in a cold water bath. Before calcination the samples were filtered, washed with distilled water and dried overnight at temperature of 105 °C. Finally, the samples were calcined in a muffle furnace at 550 °C for 6 h. The MCM-48 samples were coded as M(X) where M referred to MCM-48 and X referred to SiO_2/Al_2O_3 molar ratio.

2.7.3. Preparation of MCM-48/USY composite materials

The MCM-48 /USY composite materials were prepared by coating USY zeolite by a layer of MCM-48 mesoporous material. The preparation procedure was done according to the procedure reported by Prokesova et al., (2003) with some modifications. 3.00 g of N-hexadecyltrimethylammonium bromide (HDTMAB) was mixed with different amounts of USY zeolite (to give SiO_2/USY weight ratio in the range of 0.1-0.5) and 7 g distilled water. Hexadecyltrimethylammonium (HDTMA) ion-exchanged USY was titrated with 33 wt. % solution of NaOH to pH = 11 and added to the freshly prepared MCM-48 gel. The initial precursor of solution used for the preparation of MCM-48 mesophase had the following chemical composition: 1.0TEOS: 10.6NH_3: 46.7EtOH: 0.44HDTAMB: 423H_2O. About 3.24 of HDTMAB was dissolved in 152 ml distilled water and 45.22g ethanol, and then 12.87g of aqueous ammonia (28 wt. %) was added to the surfactant solution (HDTMAB). The formed solution was stirred and then 4.25g of TEOS and 0.04g of aluminium isopropoxide (to give Si/Al molar ratio of 125) were added.

The gel was stirred vigorously and then transferred into the Teflon bottle and aged for 24 h at 110 °C. The samples were filtered, washed with distilled water and dried at ambient temperature followed calcinations at 550 °C for 6 h in a muffle furnace. The resultant material (in Na-form) was converted to H-form by ion-exchanging with 4 M NH_4Cl aqueous solution with liquid/solid ratio of 20 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 room temperature and then calcined at 500 °C for 3 h. The composite MCM-48/USY materials were coded as C(Y) where C referred to composite MCM-48/USY and Y referred to SiO_2/USY weight ratio.

2.7.4. Impregnated catalysts

In this research, commercial NiMo/Al_2O_3 catalyst was used as cracking catalyst in preliminary study. USY zeolite was used as support for NiMo, CoMo, NiW and CoW catalysts and the composition of the catalyst was 23 wt% of MoO_3 (or WO_3) and 5.2 wt% of NiO (or CoO). A series of NiW/USY with different W and Ni concentrations were synthesized to carry out the effect of active component and promoter content. Many kinds of prepared mesoporous molecular sieve MCM-48, composite MCM-48/USY and physically mixed USY+MCM-48 were used as support for NiW. The synthesized catalysts were prepared by impregnation of the supports with aqueous solution of metal precursor using the incipient wetness method. After impregnation the sample is dried at 105 °C overnight, followed by calcinations in a muffle furnace at 500 °C for 3 h (Sato *et al.,* 1999, Hassan *et al.,* 2001).

2.8. Hydrocracking reaction

The experimental set up is shown schematically in Fig.1. Plate 1 shows the reactor system. About 30 g of desulphurized petroleum gas oil (DS-GO) sample was firstly poured into the reactor, and then the catalyst was added in different ratios from 0.00 to 0.08. Hydrogen valve was opened to develop a total hydrogen atmosphere in the range of 1-3 MPa after flushing with nitrogen. The reactor was then heated to reaction temperature in the range 300-450 °C. The reaction was carried out for a fixed period of time in the range 30-120 minutes after the reactor operating temperature and pressure were attained. At the end of the run the reactor was cooled down to room temperature under direct fan and the product was collected for analysis.

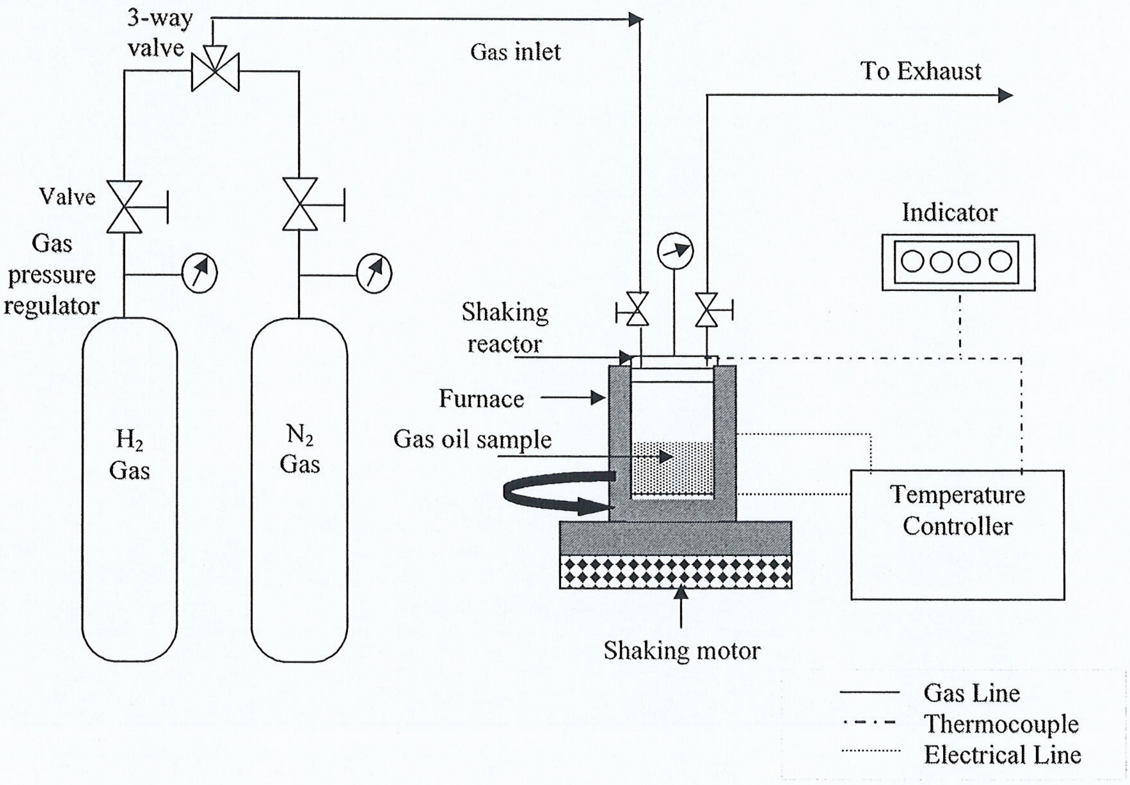

Fig. 1: Schematic diagram of experimental set up for hydrocracking of gas oil

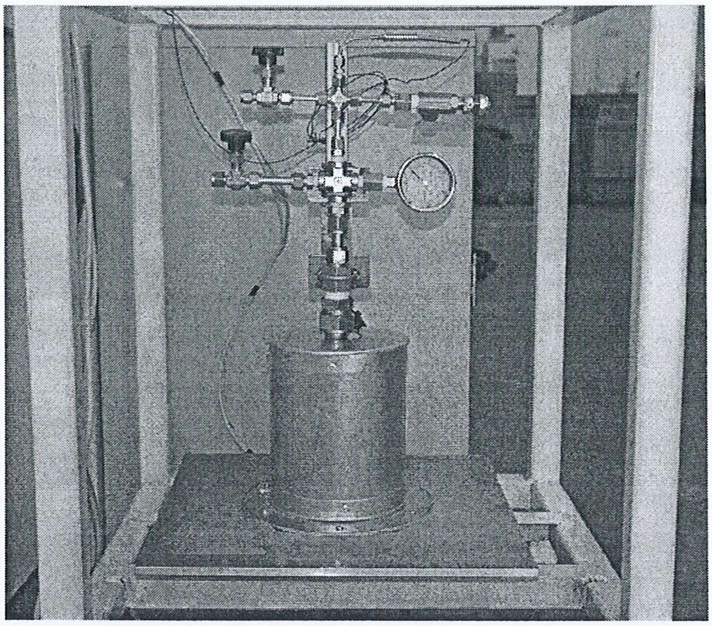

Plate 1: Photograph of the reactor system

2.9 Modeling

2.9.1. Design of experiment

Statistical design of experiment (DOE) was used to evaluate the effects of important variables in the hydrocracking of gas oil over NiW/M50 catalyst. The response surface methodology (RSM) was used to obtain the values of the total conversion, yields of gasoline, kerosene, diesel gas and coke. RSM is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response (Montgomery, 2001). The process was studied with 3^3 full factorial design using regression analysis program (Design – Expert Software, version 6.0.3, 2001). The variables identified were the reaction temperature (A), reaction time (B) and catalyst to gas oil ratio (C). The factors named and levels shown in Table 2 and Table 3 present the low and high levels which are assigned to the limit of the factorial part of the design.

Table 2: The three factors, temperature, time, catalyst to gas oil ratio and their levels

Factor	Code	Units	Low level (-1)	Medium level (0)	High level (+1)
Temperature	A	^{o}C	440	460	480
Time	B	min	20	40	60
Catalyst to GO ratio	C	-	0.02	0.04	0.06

3. Results and discussion

3.1. Hydrocracking activity of USY zeolite-based catalysts

The effect of catalyst type on the total conversion and products distribution obtained from hydrocracking of gas oil is shown in Table 4. Within experimental error, all catalysts exhibited a similar activity for the conversion of gas oil, and yielded the same quality of reaction products, namely gasoline, kerosene, diesel, gas and coke, although NiW/USY catalyst may be somewhat favoured. It is interesting to compare the activities of USY-based catalysts with that of commercial USY zeolite. Over NiW-loaded catalyst, the conversion and total distillate fuels were 15.54 and 15.77 wt%, respectively higher than USY zeolite. There are two roles of sulphided NiW, one is the supply of hydrogen to acid sites, a supply of hydrogen is essential for continuous hydrocracking, and the other role is hydrogenation of aliphatic and aromatic compounds to paraffinic and cycloparaffinic compounds, respectively (Hossain, 2006). Among the catalysts, NiW/USY catalyst showed slightly more hydrocracking activity compared to other catalysts in terms of conversion and total distillate products. The hydrocracking activities of other USY-based catalysts were slightly increased as follows, from most active to least active: NiW/USY> NiMo/USY> CoW/USY > CoMo/USY > USY.

Table 3: Design layout with coded factor levels.

Standard order	A: Temperature Code	B: Time Code	C: Catalyst to gas oil ratio Code
1	-1	-1	-1
2	-1	0	-1
3	-1	+1	-1
4	-1	-1	0
5	-1	0	0
6	-1	+1	0
7	-1	-1	+1
8	-1	0	+1
9	-1	+1	+1
10	0	-1	-1
11	0	0	-1
12	0	+1	-1
13	0	-1	0
14	0	0	0
15	0	+1	0
16	0	-1	+1
17	0	0	+1
18	0	+1	+1
19	+1	-1	-1
20	+1	0	-1
21	+1	+1	-1
22	+1	-1	0
23	+1	0	0
24	+1	+1	0
25	+1	-1	+1
26	+1	0	+1
27	+1	+1	+1
Repeated Trials			
28	0	0	0
29	0	0	0
30	0	0	0
31	0	0	0
32	0	0	0

Table 4: Gas oil hydrocracking over USY-based catalysts at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa

Catalyst	Commercial USY	NiMo/ USY	CoMo/ USY	NiW/ USY	CoW/ USY
Conversion (wt.%)	47.81	58.41	51.21	63.35	53.69
Total distilled fuels (wt.%)	36.58	49.98	39.68	52.35	41.99
Gasoline (wt.%)	8.13	14.29	13.49	11.52	12.92
Kerosene (wt.%)	7.16	8.67	4.09	5.14	10.44
Diesel (wt.%)	21.29	18.63	22.10	35.69	18.63
Gas yield (wt.%)	5.13	3.67	5.73	5.23	5.73
Gas composition (mol%)					
CH_4	0.01	0.02	0.01	0.01	-
C_2H_4	0.23	0.15	0.19	0.28	0.20
C_2H_6	38.98	39.45	37.35	42.42	41.19
C_3H_6	1.88	1.13	1.62	1.91	1.56
C_3H_8	31.50	32.68	31.27	29.15	30.32
C_4H_{10}	19.51	19.65	20.53	18.35	18.43
$C_5^{=}$	7.89	6.92	9.03	7.88	8.30
Coke yield (wt.%)	6.1	4.77	5.8	5.77	5.97

The results also show that the amount of both gas and coke obtained over all catalysts was around 8-12 wt% and the main gaseous products were hydrocarbons ethane, propane, C_4^+ and C_5^+.

3.1.1 Effect of active component and promoter concentration

A series of NiW/USY with tungsten loading in the range of 0-30 wt% and nickel loading in the range of 0-10 wt% were synthesized to find the optimum loading of active component (W) and promoter (Ni).

3.1.1. (a) Product distributions

The hydrocracking activity of NiW/USY catalysts with different nickel and tungsten concentrations was measured at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and 1000 kPa hydrogen pressure. Fig. 2 presents effect of tungsten concentration on hydrocracking of gas oil at 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. 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 68.71 and 51.38 wt%, respectively. A high catalytic activity is observed when the tungsten content reached 23 wt%, which corresponds to the present an enough amount of tungsten to a complete occupation of the edges of WS_2 slabs by the promoter.

Fig. 3 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 showed 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 63.35, 52.35, 11.52, 5.14, 35.69, 5.23 and 5.77 wt%, respectively.

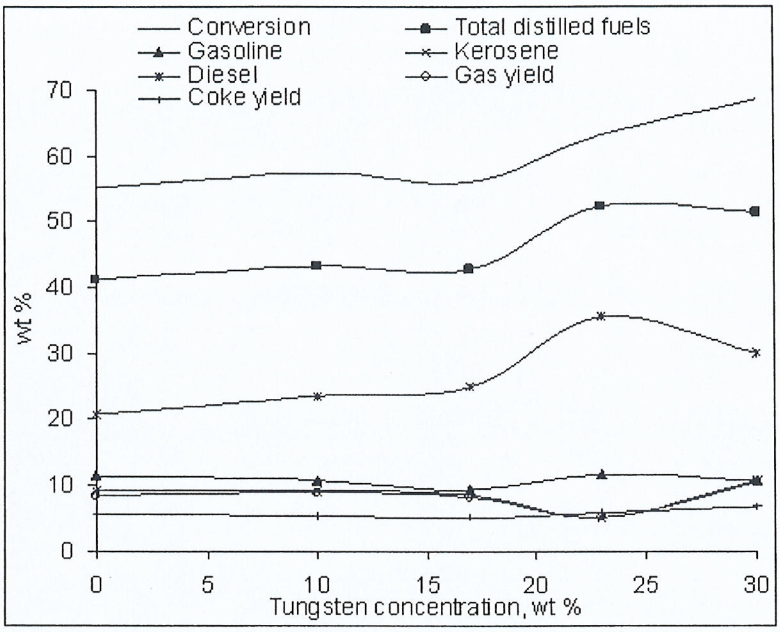

Fig. 2: Gas oil hydrocracking over NiW/USY catalyst as a function of tungsten content at a constant nickel loading of 5 wt%

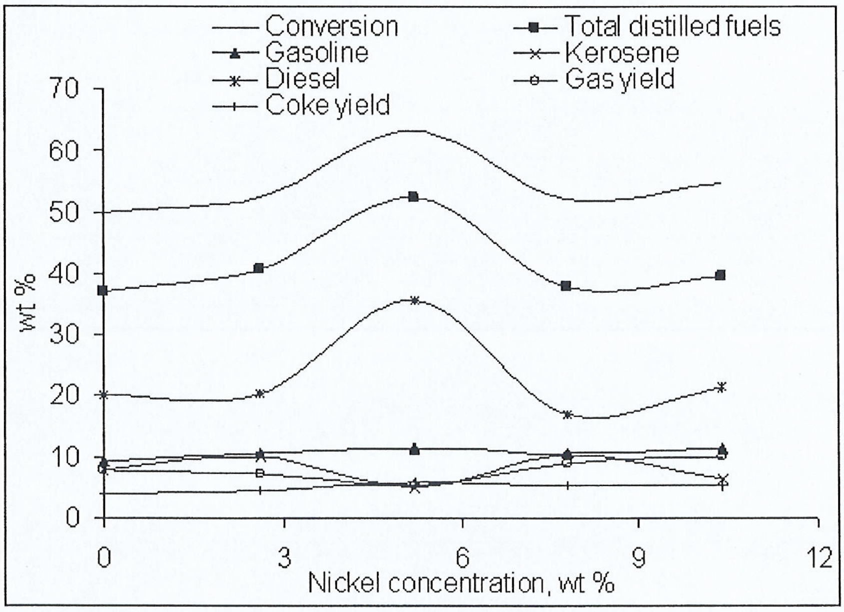

Fig. 3: Gas oil hydrocracking over NiW/USY catalyst as a function of nickel content at a constant tungsten loading of 23 wt%

These 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 rather poor dispersion which is leaded to decrease the physical properties of catalyst (surface area and pore volume decreased with increasing the metal loading).

3.2. Mesopores molecule sieve aluminosilicate materials

The synthesis of aluminium containing mesoporous MCM-48 with improved acidic characteristics is important in many catalytic applications. To improve the acidic characteristics of MCM-48, the alumina content (SiO_2/Al_2O_3 ratio) incorporated into framework was investigated. While increasing alumina content increases the activity of the catalyst, the lack of order resulting from silicate substitutions causes structure thermal instability. It is therefore important to optimise the SiO_2/Al_2O_3 ratio to achieve a reactive and stable catalyst.

3.2.1. Characterization of catalysts

Mesoporous aluminosilicate materials with three dimensional pore network MCM-48 were synthesized by the conventional hydrothermal method. The ratio of alumina to silica was varied to study the effect of the alumina on the acidity properties of synthesized materials. The X-ray diffraction (XRD) pattern of calcined MCM-48 with different SiO_2/Al_2O_3 ratios is shown in Fig. 4. It was noted that all the prepared materials exhibited characteristics diffraction lines for MCM-48. The high degree of ordering of mesoporous MCM-48 materials is confirmed by the presence of intense reflection in the mesoporous region for MCM-48. The mesophase contains two main reflections at 2θ of 2.1° and 2.7°, which confirm the mesostructural order in these samples.

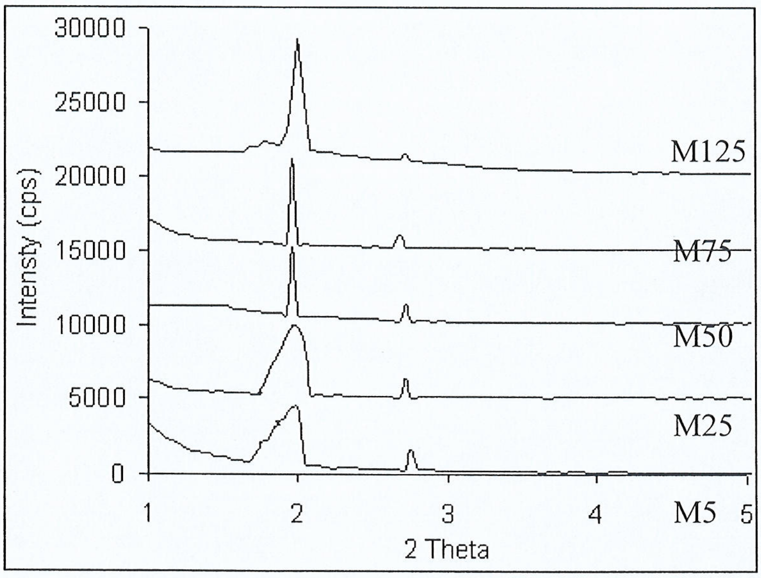

Fig. 4: XRD pattern for mesoporous molecular sieve MCM-48 with different SiO_2/Al_2O_3 ratios (M referred to MCM-48 and number referred to SiO_2/Al_2O_3 molar ratio)

The structural ordering of materials having higher SiO_2/Al_2O_3 ratio (M125) is slightly better than that of the materials having lower SiO_2/Al_2O_3 ratio (M5). Different SiO_2/Al_2O_3 ratios in the precursor may affect the formation of the MCM-48 phase. The lower SiO_2/Al_2O_3 ratio is not expected to prohibit the formation of MCM-48.

The physical properties of synthesized MCM-48 materials are presented in Table 5. It can be seen from this table that the BET surface area and pore volume were increased as alumina content decreased while, average pore diameter was decreased.

Fig. 5 shows nitrogen adsorption desorption isotherm of NiW catalysts supported on MCM-48 with different SiO_2/Al_2O_3 ratios. The isotherms were of type IV, corresponding to mesoporous solids (Halachev *et al.,* 1996). As the relative pressure increased ($P/Po > 0.2$), the isotherms exhibited sharp inflections characteristic of capillary condensation within mesopores. In any case, the sharpness of this step suggested a uniform size pore system and provided evidence of the high quality of the catalysts. The slope of the adsorption isotherm in the 0.3 to 0.8 partial pressure region for samples having higher SiO_2/Al_2O_3 ratio (NiW/M125 and NiW/M78) was comparatively greater than that having higher SiO_2/Al_2O_3 ratio catalysts. This indicated that the particle size and particle aggregation probably differed with SiO_2/Al_2O_3 ratios. Thus the change in the hysteresis loop in the 0.35 to 0.6 partial pressure region was associated with framework mesoporosity, whereas the hysteresis loop at high partial pressure ($P/Po > 0.8$) was indicative of textural mesoporosity and/or macroporosity. A narrower pore distribution was observed with decrease SiO_2/Al_2O_3 ratios (Fig. 6).

Fig. 7 and 8 present the acidity results obtained from temperature programmed desorption (TPD) using TGA for MCM-48 and NiW/MCM-48 as a function of SiO_2/Al_2O_3 ratio, respectively. The total acidity and type of acid sites (weak and strong) were found to increase with Al content until SiO_2/Al_2O_3 ratio of 50 then decreased. The incorporation of Al into the framework generated acid sites which were able to interact with the base. Higher Al content did not show higher acidity related to the low crystallinity and suggesting that not all alumina was incorporated into the framework.

Fig. 9 and 10 show the experimental results of thermal stability analysis of calcined MCM-48 and NiW/MCM-48, respectively. According to the TGA curves, all synthesized materials showed very high thermal stability up to 700 °C and the weight loss below 100 °C is attributed to physically adsorbed water in the porous materials.

Scanning electron microscopy (SEM) of MCM-48 and NiW/MCM-48 with silica/alumina ratio of 50 is shown in Fig. 11 and 12, respectively. The SEM images show

Table 5: BET surface area, pore volume, average pore diameter of MCM-48 materials

Catalyst	Surface area, m^2/g	Mesoporous area, %	Microporous area, %	Pore volume, cm^3/g	Average pore size (APS), nm
M5	185.0	44.7	55.3	0.194	4.20
M25	250.4	40.5	59.5	0.230	3.67
M50	462.0	34.7	65.3	0.410	3.55
M75	558.6	32.9	67.1	0.457	3.27
M125	814.0	30.0	70.0	0.657	3.23
NiW/M5	122	91.9	8.1	0.172	5.65
NiW/M25	147	88.3	11.7	0.196	5.34
NiW/M50	187	85.6	14.4	0.218	4.68
NiW/M75	209.3	82.7	17.3	0.226	4.32
NiW/M125	253.9	80.1	19.9	0.231	3.64

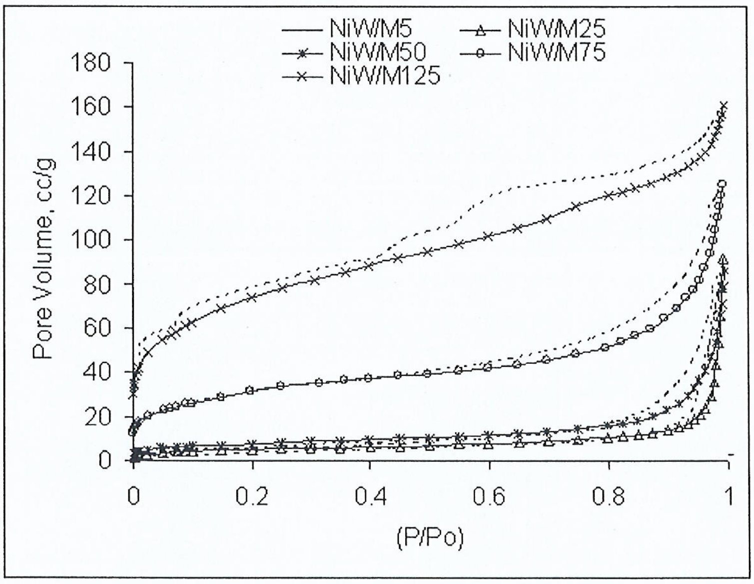

Fig. 5: Adsorption (solid line) and desorption (dotted line) isotherm of NiW catalysts supported on MCM-48 with different SiO_2/Al_2O_3 ratios

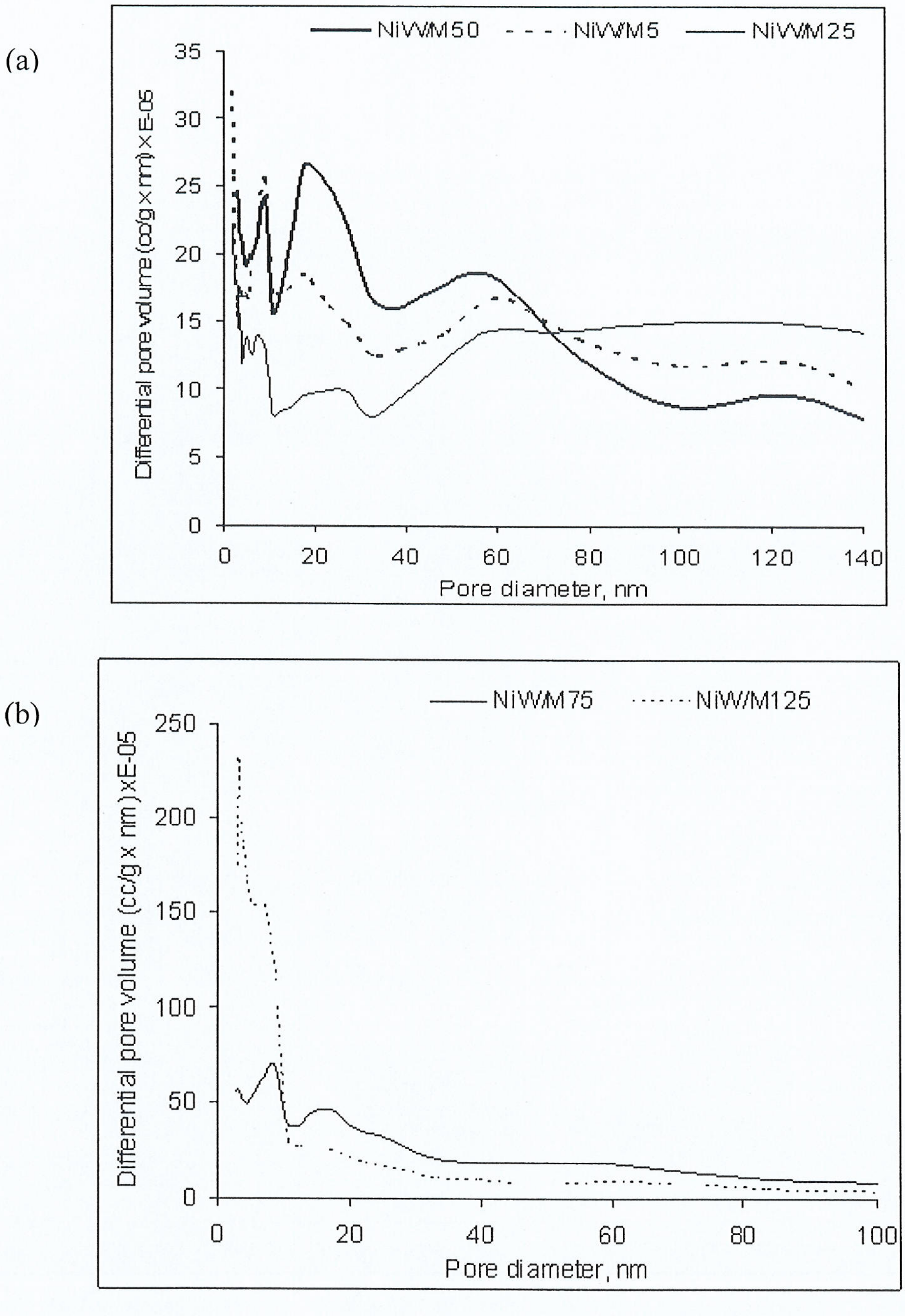

Fig. 6: Pore size distribution of NiW catalysts supported on MCM-48 with different SiO_2/Al_2O_3 ratios

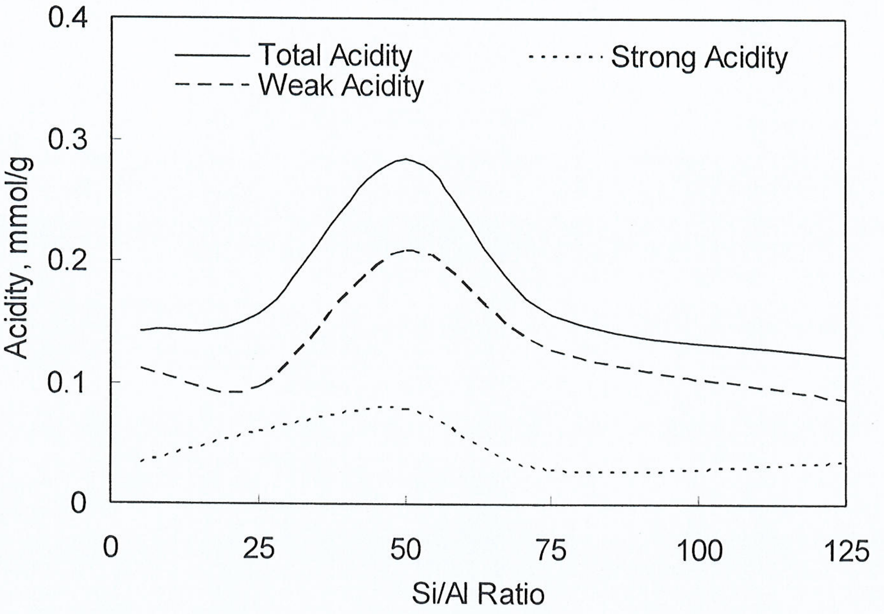

Fig. 7: TGA-TPD acidity for MCM-48 supports versus SiO_2/Al_2O_3 ratios

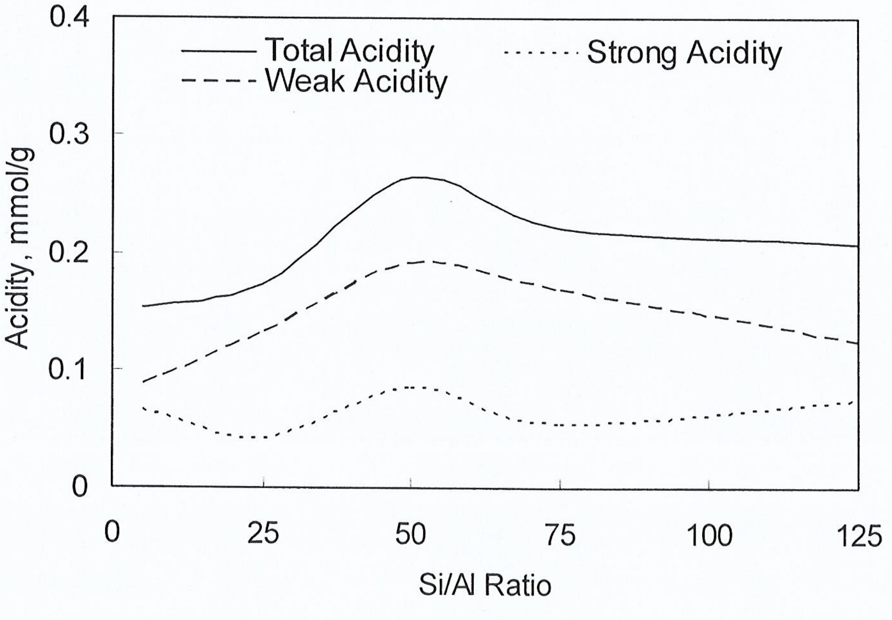

Fig. 8: TGA-TPD acidity for NiW/MCM-48 catalysts versus SiO_2/Al_2O_3 ratios

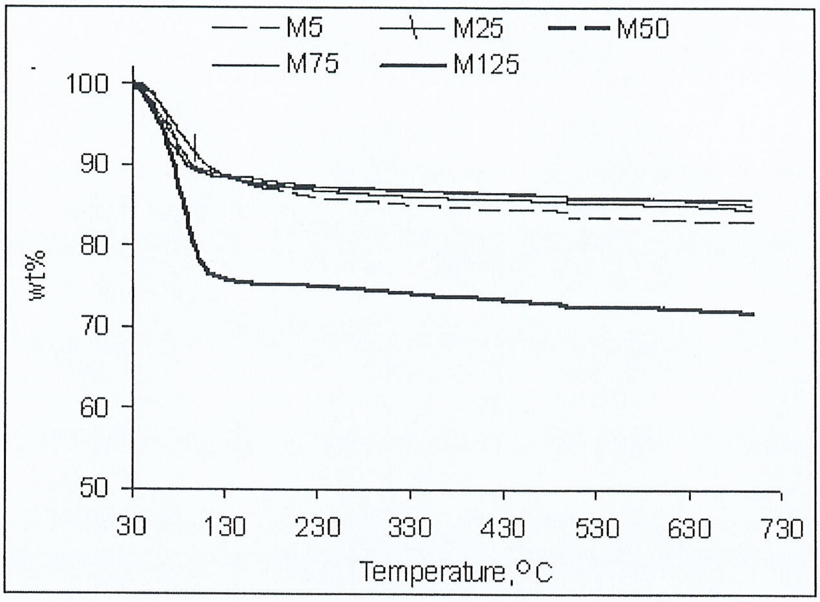

Fig. 9: TGA thermal stability results for MCM-48 with different SiO_2/Al_2O_3 ratios

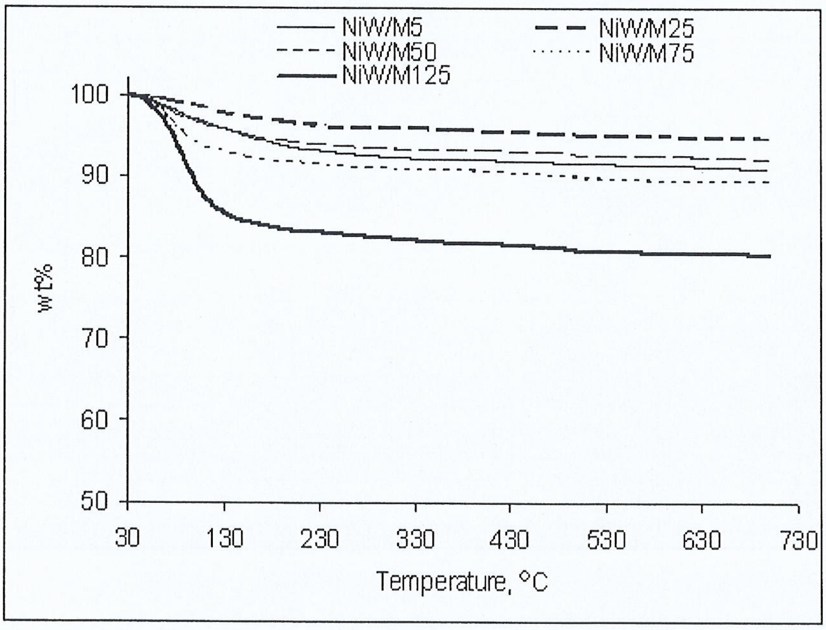

Fig. 10: TGA thermal stability results for NiW/MCM-48 with different SiO_2/Al_2O_3 ratios

that shape and size of crystalline particles were not uniform. For comparison, large sausage-like particles and big pore size were observed in the SEM image of MCM-48 (Figure 4.28), while the NiW metals appeared to be primarily randomly distributed on the MCM-48 support and both fill up and plug some of pores.

The TEM images of NiW/MCM-48 with different silica/alumina ratios are presented in Fig. 13 and 14. The structural characteristic of mesoporous molecular sieve MCM-48 can be observed clearly in Fig. 13. In addition, the form unhomogeneity with some spherical compounds presented in NiW/MCM-48 catalysts was noticed and found to increase with increase SiO_2/Al_2O_3 ratio. Furthermore, the TEM image showed the morphology of the NiW/MCM-48 catalyst and NiW particles attached on MCM-48 were clearly observed in Fig. 14.

3.2.2. Activity testing

The NiW/MCM-48 catalysts with different silica/alumina ratios were tested in hydrocracking of gas oil at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa. The hydrocracking results of MCM-48 and NiW/MCM-48 are presented in Tables 6 and 7, respectively.

These results show that MCM-48 materials were active catalysts in gas oil hydrocracking. Clearly, the cracking activity of NiW/MCM-48 catalysts is high in comparison to the unloaded MCM-48. This is due to the present the active component (W) and promoter (Ni). The active component (W) responsible for the principal chemical reaction, saturate aromatics in the feed, saturate olefins formed in the cracking, and protects the catalyst from poisoning by the coke. The role of the promoter (Ni) is to

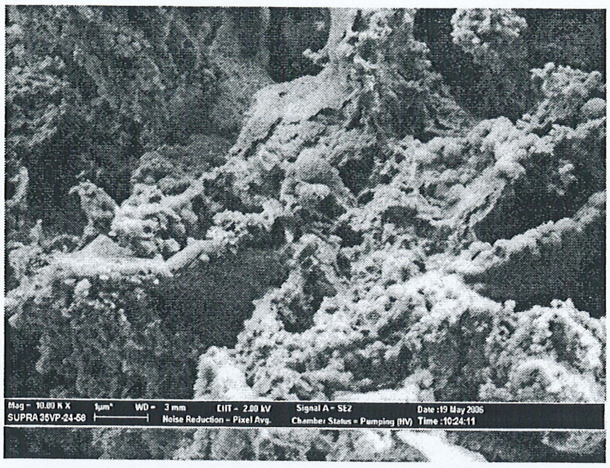

Fig. 11: Scanning electron micrographs of M50 support;
magnification is 10000:1

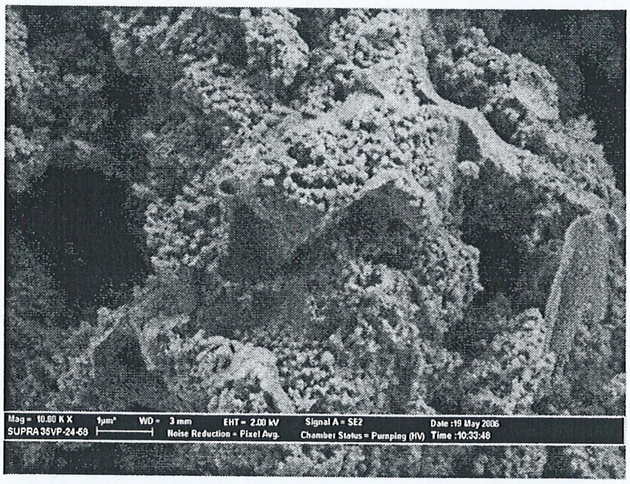

Fig. 12: Scanning electron micrographs of NiW/M50 catalyst; magnification is 10000:1

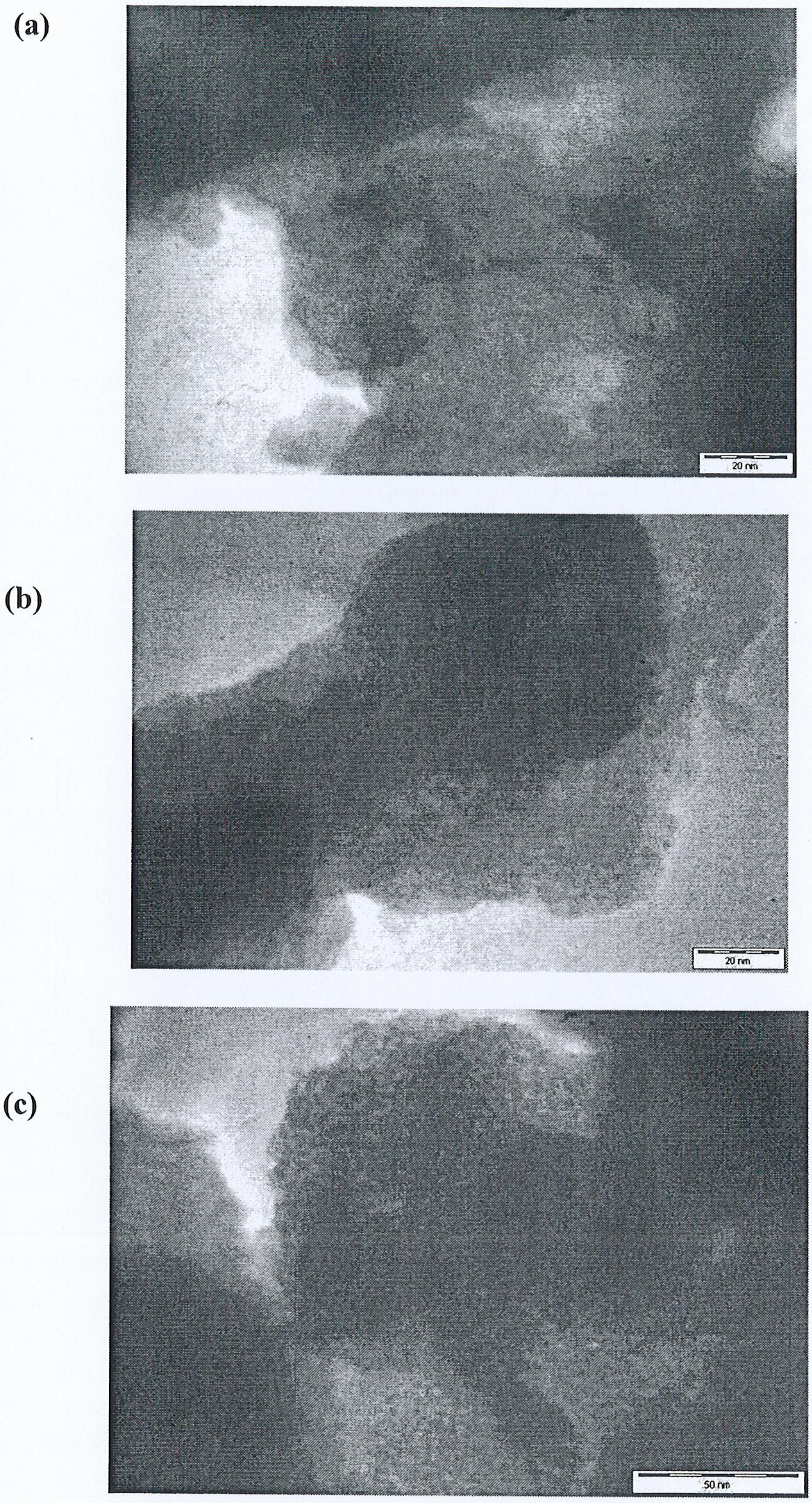

Fig 13: TEM images of NiW/MCM-48 with different SiO_2/Al_2O_3 ratios: (a) $SiO_2/Al_2O_3 = 50$, (b) $SiO_2/Al_2O_3 = 75$, (c) $SiO_2/Al_2O_3 = 125$

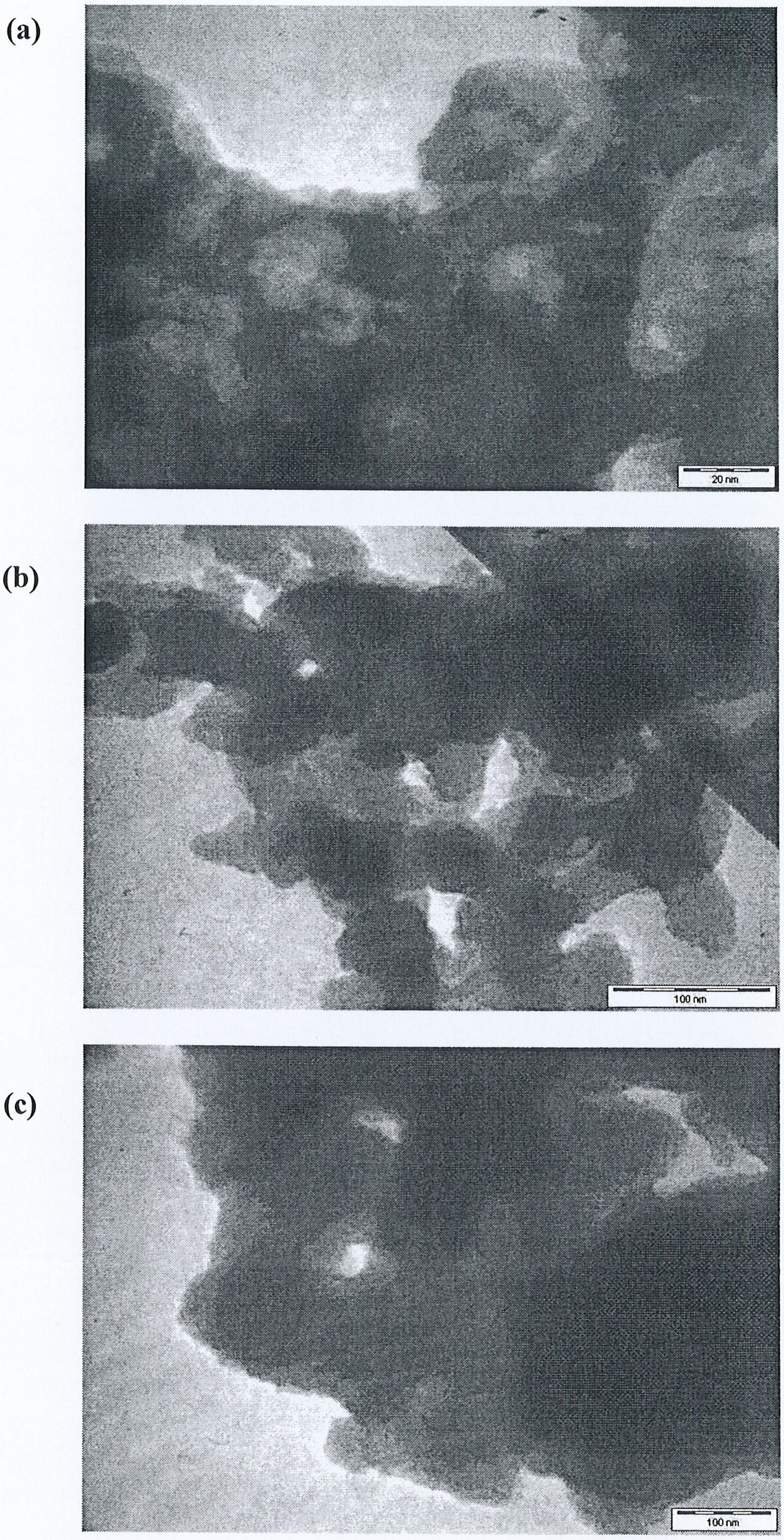

Fig. 14: TEM micrograph of NiW particles attached on MCM-48 with different SiO_2/Al_2O_3 ratios (a) $SiO_2/Al_2O_3 = 50$, (b) $SiO_2/Al_2O_3 = 75$, (c) $SiO_2/Al_2O_3 = 125$

Table 6: Gas oil hydrocracking over MCM-48 with different SiO_2/Al_2O_3 ratios at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa

Catalyst	M5	M25	M50	M75	M125
Conversion (wt.%)	42.56	43.61	50.23	45.11	43.35
Total distilled fuels (wt.%)	33.09	32.41	38.83	32.31	31.95
Gasoline (wt.%)	6.13	8.42	7.90	9.10	8.83
Kerosene (wt.%)	6.92	6.11	4.71	5.15	6.29
Diesel (wt.%)	20.04	17.88	26.22	18.06	16.83
Gas yield (wt.%)	5.77	6.73	7.4	8.27	7.7
Gas composition (mol%)					
CH_4	-	0.05	0.01	-	0.02
C_2H_4	0.57	0.27	0.32	0.25	0.25
C_2H_6	22.94	52.65	22.70	25.43	36.59
C_3H_6	5.43	1.58	3.40	2.32	2.18
C_3H_8	21.42	27.23	34.68	28.34	34.15
C_4H_{10}	23.91	13.38	26.62	26.64	23.42
$C_5^{=}$	25.73	4.84	12.27	17.02	3.39
Coke yield (wt.%)	3.7	4.47	4	4.53	3.7

Table 7: Gas oil hydrocracking over NiW/MCM-48 with different SiO_2/Al_2O_3 ratios at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa

Catalyst	NiW/M5	NiW/M25	NiW/M50	NiW/M75	NiW/M125
Conversion (wt.%)	52.61	62.49	64.31	60.23	59.44
Total distilled fuels (wt.%)	36.61	48.13	51.48	46.03	44.97
Gasoline (wt.%)	9.14	9.48	15.58	12.30	11.22
Kerosene (wt.%)	10.71	10.00	6.50	9.99	9.31
Diesel (wt.%)	16.76	28.65	29.40	23.74	24.44
Gas yield (wt.%)	11.00	10.13	8.83	10.37	10.80
Gas composition (mol%)					
CH_4	0.01	0.05	0.01	0	0.01
C_2H_4	0.20	0.27	0.16	0.29	0.20
C_2H_6	51.95	51.65	42.08	46.32	47.52
C_3H_6	1.42	1.58	1.32	1.63	2.88
C_3H_8	29.69	27.23	34.03	30.09	30.73
C_4H_{10}	16.73	15.38	22.4	18.93	18.66
$C_5^{=}$	0	3.84	0	2.74	0
Coke yield (wt.%)	5.00	4.23	4.00	3.83	3.67

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 from the sulphided catalysts, thus leading to more numerous of active sites in the reductive atmospheric of the hydrocracking processes.

The total conversion and the product distribution were found to increase with decrease SiO_2/Al_2O_3 ratio till SiO_2/Al_2O_3 ratio of 50 then decreased. The acidity and porosity of catalysts influenced the product distribution obtained from the catalytic hydrocracking. NiW/MCM-48 with SiO_2/Al_2O_3 ratio of 50 (NiW/M50) possessed a high acidity, therefore, gave higher gas oil conversion and distilled products. It gave 64.31, 51.48, 15.58, 6.50 and of total conversion, total distilled products, gasoline, kerosene and diesel, respectively. The yield of coke and gaseous products was in good agreement with the acidity changes happened during the change of SiO_2/Al_2O_3 ratio. This confirms the role of the strength of acid sites on the cracking reaction.

3.3. Meso/Microporous composite materials

To overcome the limitations of microporous zeolites, USY zeolite was coated with a layer of MCM-48 mesoporous material at different meso/microporous ratios (SiO_2/USY ratios of 0.1, 0.2, 0.3, 0.4, 0.5). These composite MCM-48/USY materials were coded as C(Y) where C referred to composite MCM-48/USY and Y referred to SiO_2/USY weight ratio. The prepared catalysts were characterized and tested for hydrocracking of gas oil at reaction temperature of 450 ^{o}C, contact time of 90 min and catalyst to gas oil ratio of 0.04. Finally, the obtained results from hydrocracking of gas oil over composite MCM-48/USY catalysts were compared with those obtained over physically mixed USY and

MCM-48 catalysts. The physically mixed samples were coded as Mix(Z) where Z referred to MCM-48/(MCM-48+USY) weight percentage.

3.3.1. Characterization of catalysts

Fig. 15 presents X-ray diffraction (XRD) traces of samples prepared by coating USY zeolite by a layer of MCM-48 mesoporous material. XRD analysis shows one new peak at 2θ value of 2 in the addition of the USY pattern which did not change from the original pattern. The position of this new peak was in mesophase range (2θ value of 2) which confirmed that the mesophase species are present in all prepared composite materials. The peak intensity is increased with increasing SiO_2/USY ratio due to increase MCM-48 in the prepared composite.

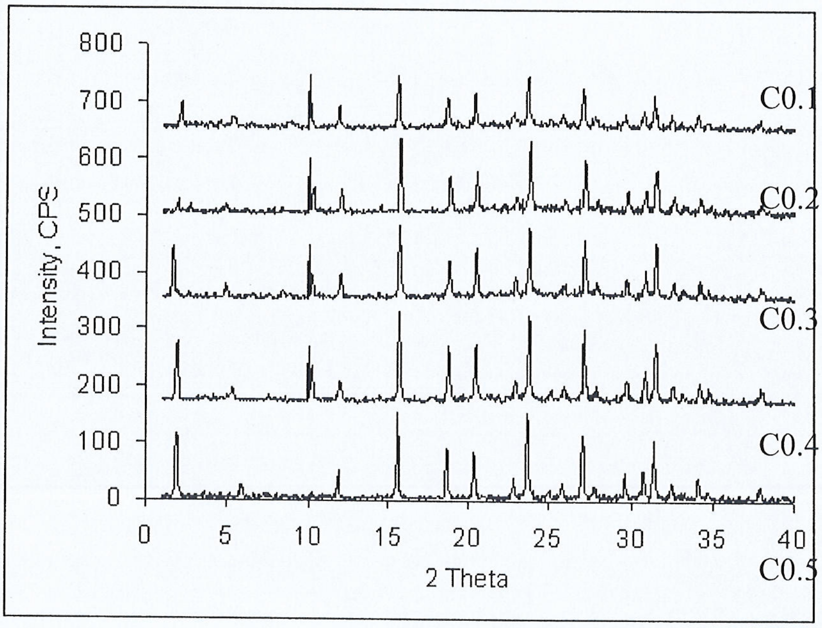

Fig. 15: XRD pattern for composite MCM-48/USY materials with different SiO_2/USY ratios

The surface characteristics and porosity in terms of BET surface area, pore volume and average pore diameter of the prepared composite catalysts are given in Table 8. The surface area, average pore diameter and pore volume values obtained are of the catalysts containing USY zeolites and mesoporous MCM-48 material and thus represent the properties of the composite supports. The catalysts loaded with NiW showed lower surface area and pore volume compared to unloaded supports. Similarly, catalysts prepared with higher SiO_2/USY ratio showed lower surface area and pore volume as compared to those having lower SiO_2/USY ratios. This is due to decrease the amount of USY zeolites in prepared composite which is having higher surface area and pore volume than MCM-48.

Table 8: The surface characteristics of the prepared composite materials

Catalyst	Surface area, m^2/g	Mesoporous area, %	Microporous area, %	Pore volume, cm^3/g	Average pore size (APS), nm
C0.1	689.95	17.93	82.07	0.3738	2.167
C0.2	596.35	18.82	81.18	0.3261	2.187
C0.3	586.41	51.01	48.99	0.3228	2.202
C0.4	537.7	69.69	30.31	0.3048	2.267
C0.5	494.12	87.83	12.17	0.2837	2.297
NiW/C0.1	433.5	32.81	67.19	0.2683	2.476
NiW/C0.2	356.77	62.92	37.08	0.2364	2.560
NiW/C0.3	299.17	77.12	22.88	0.2041	2.729
NiW/C0.4	287.14	85.41	14.59	0.1972	2.747
NiW/C0.5	228.66	89.23	10.77	0.1589	2.780

Fig. 16 shows the N_2 adsorption-desorption isotherms of NiW supported on MCM-48/USY composite catalysts obtained from N_2 adsorption. It is seen that adsorption capacity is increased with increase SiO_2/USY ratio. According to the IUPAC definition, mesoporous materials exhibit a type IV adsorption-desorption isotherm. Depending on the pore size, a sharp increase is seen at relative pressures from 0.25 to 0.5. This corresponds to capillary condensation of N_2 in the mesopores. The pore size distributions of composite catalysts are illustrated in Fig. 17. As shown, all catalysts exhibit two main pore size peaks occur centered at 2 and 7-15 nm. The peak size in mesoporous range is enlarged with increase SiO_2/USY ratio due to increase amount of mesophase (MCM-48) in prepared materials.

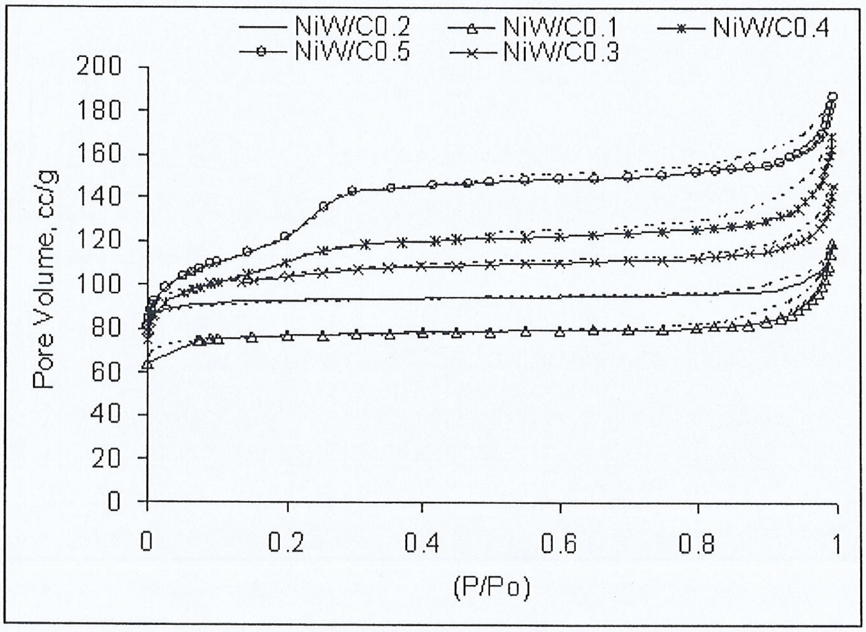

Fig. 16: Adsorption (solid line) and desorption (dotted line) isotherm of NiW catalysts supported on MCM-48/USY with different SiO_2/USY ratios

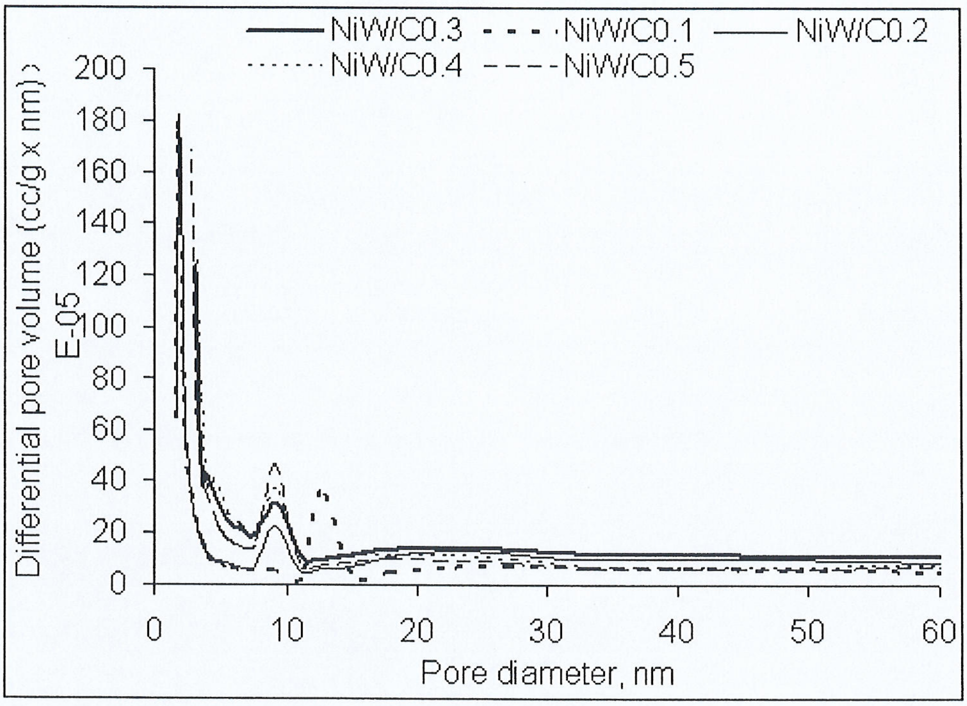

Fig. 17: Pore size distribution of NiW catalysts supported on MCM-48/USY with different SiO_2/USY ratios

The temperature programmed desorption (TPD) using TGA of NiW/MCM-48/USY (NiW/C0.1-C0.5) and MCM-48/USY (C0.1-C0.5) composite catalysts with different SiO_2/USY ratios are presented in Fig. 18 and 19, respectively. For all catalysts, the major peaks were found at 200-300 °C. This range has been assumed to be the large amount of weak acid sites (Lewis type). Fig. 20 and 21 present amounts of weak and strong acid sites of NiW/MCM-48/USY and MCM-48/USY composite catalysts as a function of SiO_2/USY ratio, respectively. In contrast to the SiO_2/USY ratio, all catalysts show similar amount of strong acid sites (Bronsted) and there is no significant differences between all catalysts were observed. Total and weak acid sites were increased with decreasing SiO_2/USY ratio until SiO_2/USY ratio of 0.2- 0.3 then became constant and this was due to the increment of USY zeolites concentration in the composite materials.

Scanning electron microscopy images (SEM) of C0.5 and NiW/C0.5 composite catalyst are shown in Fig. 22 and 23, respectively. SEM was carried out in order to observe the changes in the morphology and surface texture of coated materials. The SEM images of composite material show that there was an overgrowth of non-uniform cabbage-like crystals on USY zeolites. The SEM micrograph of unloaded materials indicated smooth and almost uniform particles.

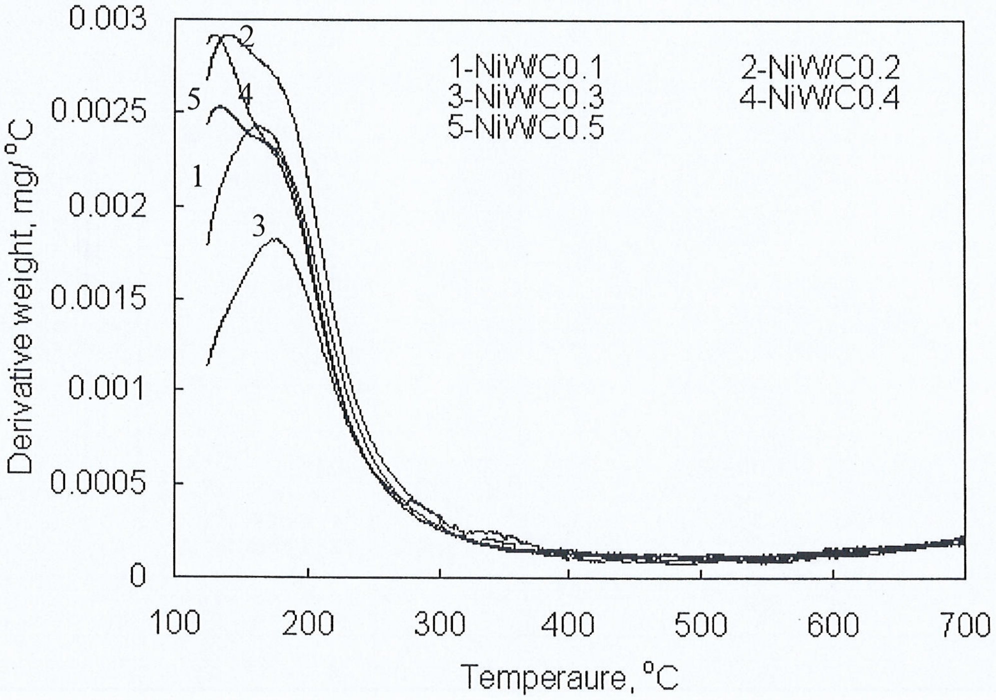

Fig. 18: TGA-TPD acidity types of NiW supported on MCM-48 /USY composite catalysts

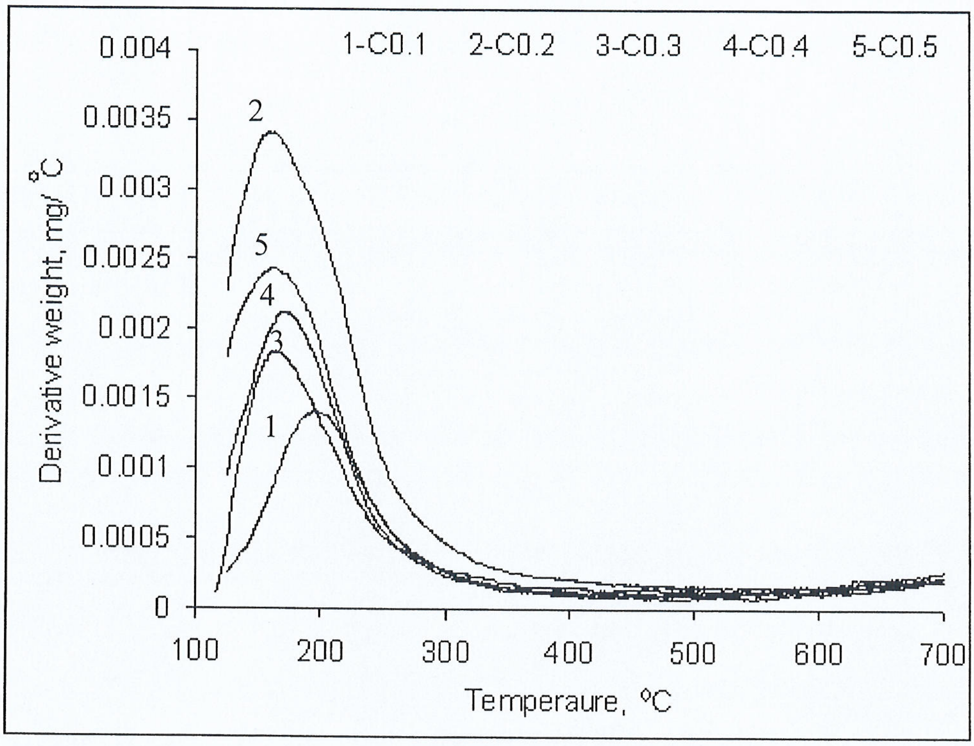

Fig. 19: TGA-TPD acidity types of MCM-48/USY composite supports

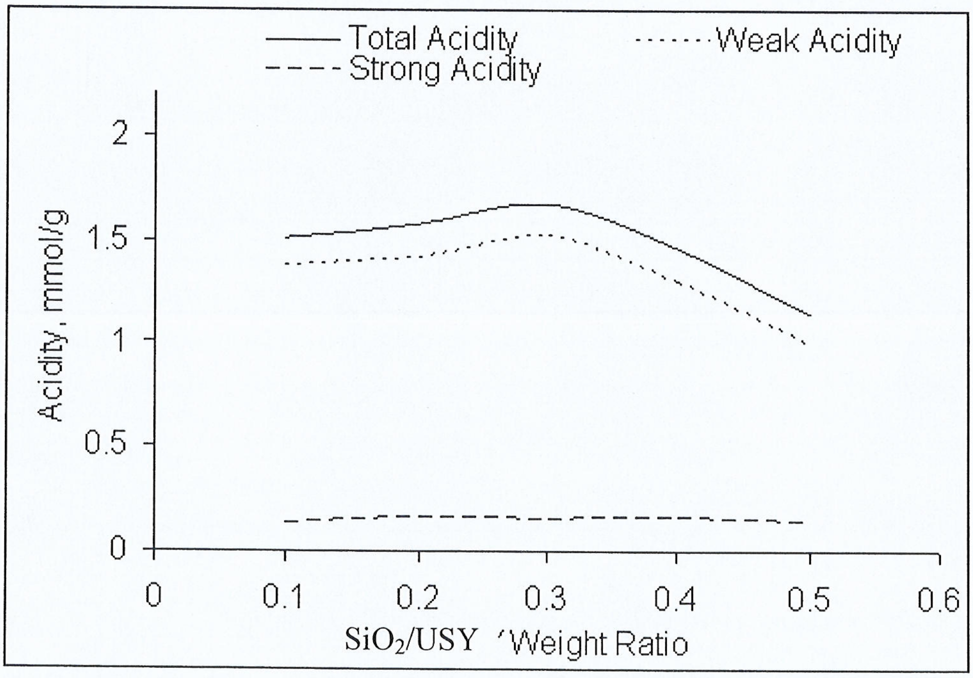

Fig. 20 TGA-TPD acidity for NiW/MCM-48-USY composite catalysts

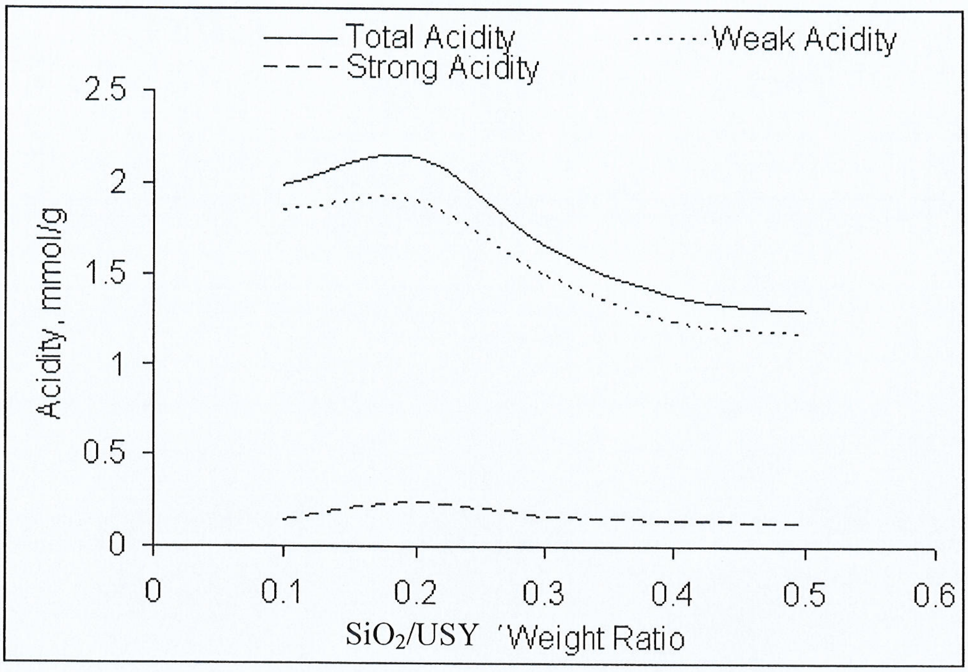

Fig. 21 TGA-TPD acidity for MCM-48-USY composite supports

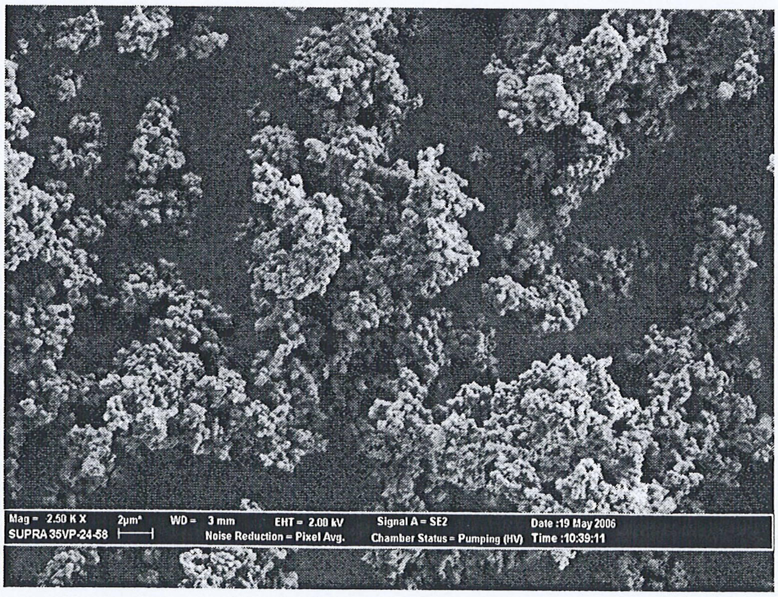

Fig. 22: Scanning electron micrographs of C0.5 support; magnification is 2500:1

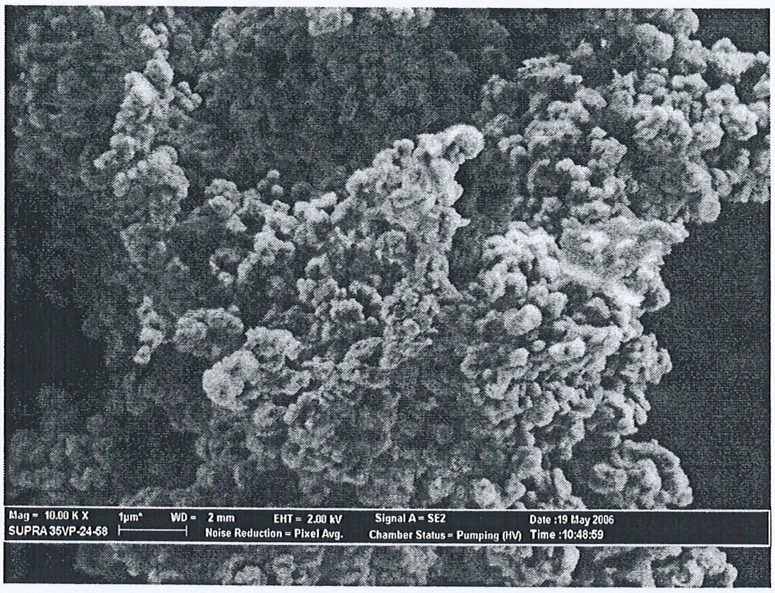

Fig. 23: Scanning electron micrographs of NiW/C0.5 catalyst; magnification is 10000:1

The transmission electron microscopy (TEM) images of NiW/MCM-48-USY composite catalysts with different SiO_2/USY ratios are shown in Fig. 24 and 25. The TEM image shows a highly ordered pore arrangement in middle regions (region M). However, the pores are orientated at different angles in different areas. For example, in upper region (region U) the pores are oriented at an angle to the plane of the image whereas in lower region (region L), they are oriented parallel to the image. The composite catalysts are composed of a uniform array of pores which are curved at the centre of the image. TEM examination of the synthesized material showed that MCM-48 (light colour) was indeed situated on the outer surface of USY crystals (dark colour).

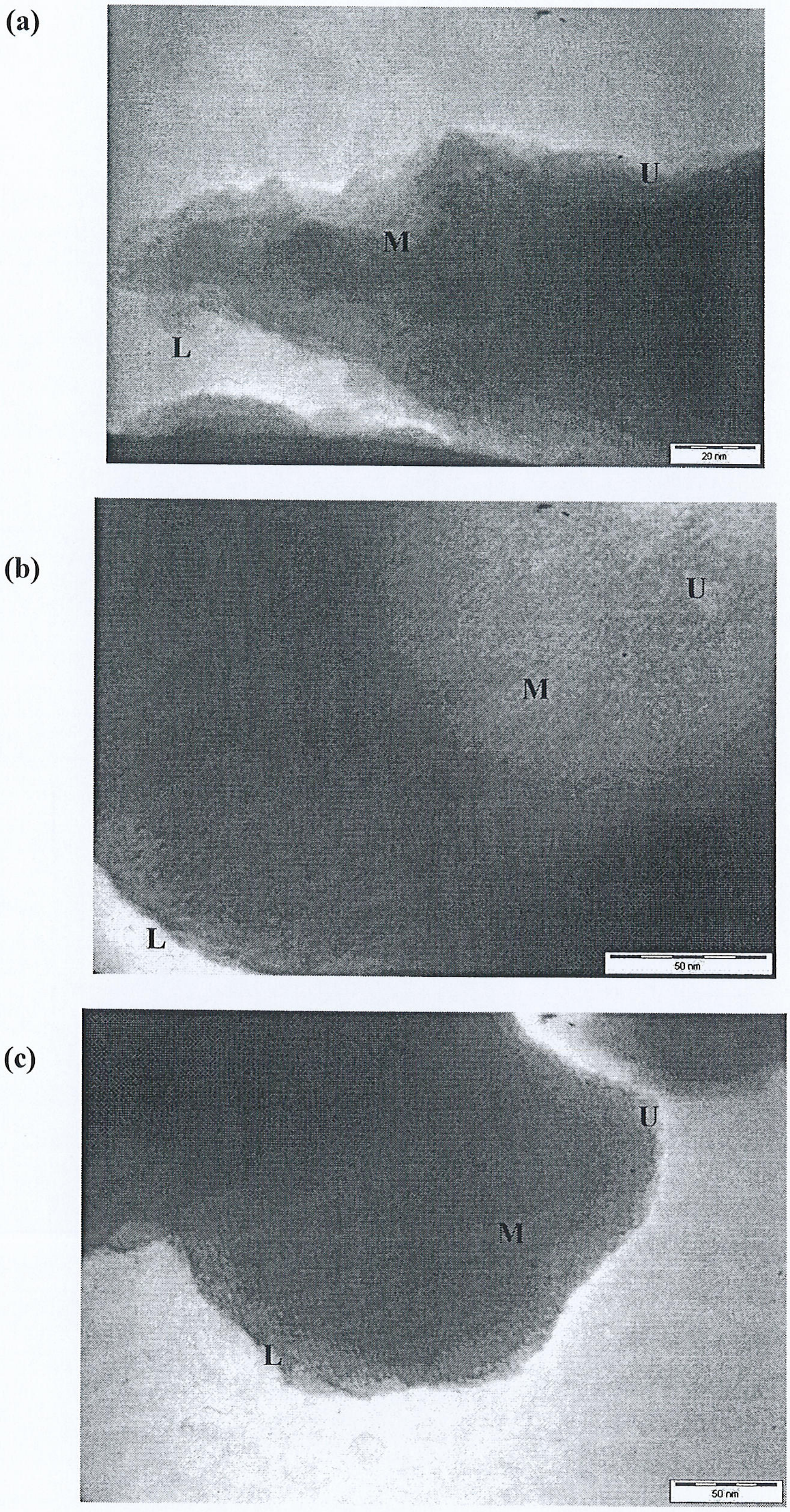

Fig. 24: TEM images of NiW/MCM-48-USY with different SiO_2/USY ratios :(a) SiO_2/USY = 0.2, SiO_2/USY = 0.4, SiO_2/USY = 0.5
U: upper region, M: middle region, L: lower region

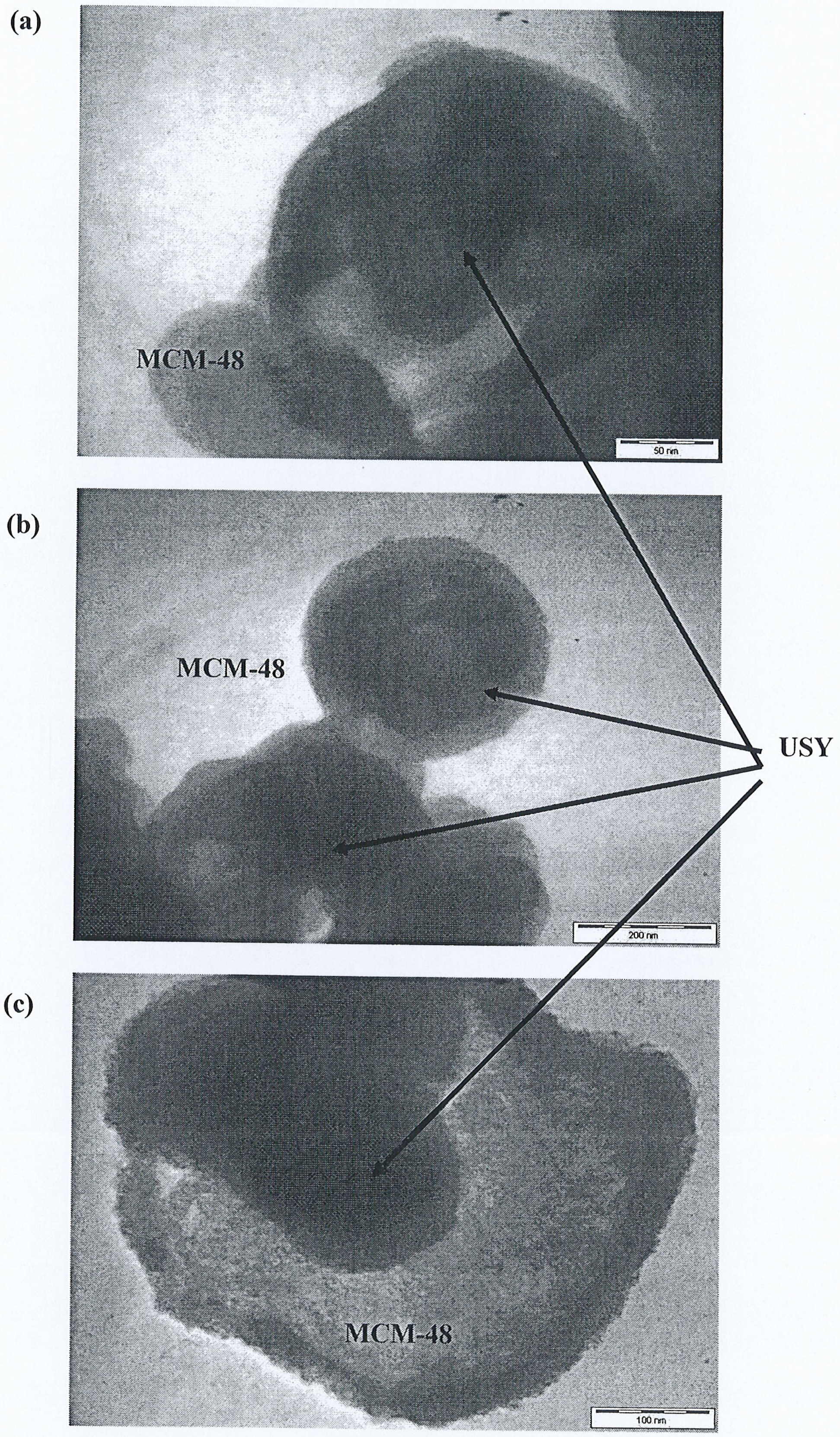

Fig. 25: TEM micrograph of MCM-48 coated USY with different SiO_2/USY ratios :(a) SiO_2/USY = 0.2, SiO_2/USY = 0.4, SiO_2/USY = 0.5

The results of thermogravimetric analysis (TGA) of the composite MCM-48/USY samples and NiW/MCM-48/USY are shown in Fig. 26 and 27, respectively. Furthermore, all samples showed similar results in TGA analysis. Two steps can be observed in these Figures. The first step, centered at temperature of 110 °C, is associated with physically adsorbed water, constituting about 15% weight loss. The second step in the ATG curve attributed to the main species of the composite materials. These results confirmed that synthesized catalysts posses very high the thermal stability.

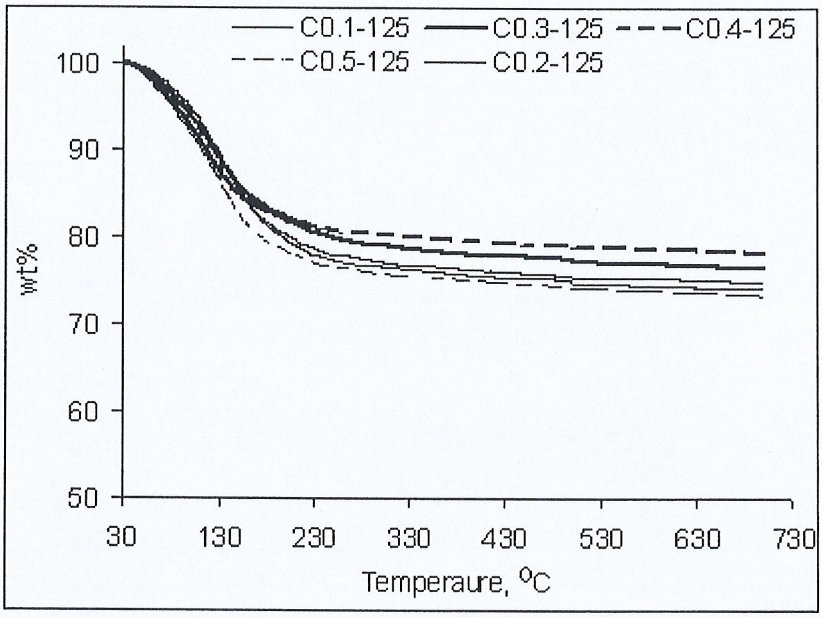

Fig. 26: TGA thermal stability results for MCM-48-USY composite supports with different SiO_2/USY ratios

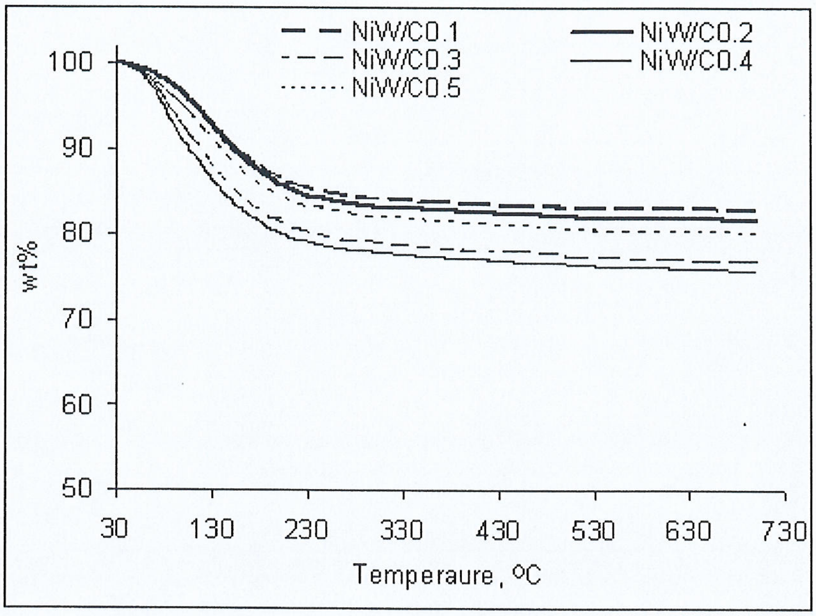

Fig. 27: TGA thermal stability results for NiW/MCM-48-USY composite catalysts with different SiO_2/USY ratios

3.3.2. Catalysts performance evaluation

The performance of prepared NiW/MCM-48-USY composite catalysts were evaluated in hydrocracking of gas oil at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa. The hydrocracking products of gas oil using NiW/MCM-48-USY composite catalysts were analyzed for boiling range distribution. The results presented in Tables 9 and 10 indicate a marked degree of conversion of gas oil feed into gasoline, kerosene, and diesel. The hydrocracking activity of all catalysts was found to increase with SiO_2/USY ratio. The amounts of gasoline, kerosene, and diesel increased with the SiO_2/USY ratio for all catalysts, while the amounts of coke decreased. This is attributed to the good balance between acidity of USY zeolites and high pore size of MCM-48. Another possible reason of higher activity might be less coke deposition on the catalysts. The amount of coke deposition on catalysts with higher SiO_2/USY ratio was less compared to that of low SiO_2/USY ratio. The less coking was probably due to the lower acidity of catalysts with higher SiO_2/USY ratio.

Table 9: Gas oil hydrocracking over MCM-48-USY composite catalysts with different SiO_2/USY ratios at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa

Catalyst	C0.1	C0.2	C0.3	C0.4	C0.5
Conversion (wt.%)	52.41	55.20	60.92	62.82	65.69
Total distilled fuels (wt.%)	36.41	38.53	44.62	47.19	50.92
Gasoline (wt.%)	10.54	10.64	11.19	14.95	14.40
Kerosene (wt.%)	6.13	5.78	23.70	17.74	18.99
Diesel (wt.%)	19.74	22.11	9.73	14.50	17.53
Gas yield (wt.%)	10.00	11.00	11.30	10.90	10.43
Gas composition (mol%)					
CH_4	0.00	0.00	0.00	0.00	0.00
C_2H_4	0.27	0.22	0.19	0.22	0.20
C_2H_6	37.61	52.04	43.05	50.31	54.20
C_3H_6	2.18	1.46	1.55	1.52	1.29
C_3H_8	34.99	29.92	33.90	29.78	29.11
C_4H_{10}	24.95	16.36	21.31	18.17	15.20
$C_5^{=}$	0.00	0.00	0.00	0.00	0.00
Coke yield (wt.%)	6.00	5.67	5.00	4.73	4.34

Table 10: Gas oil hydrocracking over NiW/MCM-48-USY composite catalysts with different SiO_2/USY ratios at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa

Catalyst	NiW/ C0.1	NiW/ C0.2	NiW/ C0.3	NiW/ C0.4	NiW/ C0.5
Conversion (wt.%)	57.64	64.49	66.96	68.03	69.74
Total distilled fuels (wt.%)	40.97	48.16	50.32	53.19	56.07
Gasoline (wt.%)	11.58	12.89	13.72	14.47	13.79
Kerosene (wt.%)	6.16	8.77	5.81	8.69	12.97
Diesel (wt.%)	23.23	26.50	30.79	30.03	29.31
Gas yield (wt.%)	10.34	10.06	10.44	10.57	10.03
Gas composition (mol%)					
CH_4					
C_2H_4	0.00	0.00	0.00	0.00	0.00
C_2H_6	0.33	0.19	0.18	0.17	0.17
C_3H_6	47.65	48.45	36.56	42.93	45.31
C_3H_8	1.63	1.62	1.84	2.58	1.37
C_4H_{10}	30.41	29.63	35.17	30.56	33.4
$C_5^{=}$	19.98	19.91	26.25	20.95	19.75
	0.00	0.00	0.00	2.81	0.00
Coke yield (wt.%)	6.33	6.27	6.20	4.27	3.64

Hence, the catalyst surface remained clean and active for further reactions. The hydrocracking activities of unloaded catalysts were found lower than those of NiW-based catalysts. This indicates that the higher hydrogenation activity was achieved by the action of NiW metals. The presence of NiW metals provides sufficient amounts of reactive hydrogen and instantaneously hydrogenates the cracking intermediates produced by the cracking reaction and prevents further cracking to produce lower hydrocarbons (Hossain, 2006). Generally, for all the catalysts, the gas production was found to be constant. Among the gas product components, the C_2H_6 was found to be in highest quantity followed by C_3H_8 and C_4H_{10}.

It is interesting to compare hydrocracking activity of NiW/MCM-48-USY composite catalysts with that of physically mixed USY and MCM-48 catalysts at different mixing weight percentages (Mix = 0, 20, 40, 60, 80, 100). Table 4.11 shows total conversion and yield of products obtained over NiW/Mix catalyst at the same operating conditions. The NiW/MCM-48-USY composite catalysts show higher conversion than the physically mixture. It can also be seen that NiW/MCM-48-USY is more selective to the light products than NiW/Mix. These results would be attributed to the introduction into the composite mesopore walls of the secondary building unit characteristic of USY zeolites which gives rise to the higher hydrothermal stability and more strong acid sites. Beside, the higher activity of NiW/MCM-48-USY composite catalysts might be caused by the faster diffusions of reactant in composite than in physically mixture because the composite can provide more interconnected pores and its acid sites are more accessible (Wang *et al.,* 2005).

Table 4.11: Gas oil hydrocracking over physically mixed NiW/Mix catalysts with different MCM-48/(MCM-48-USY) percentages (Mix = 0, 20, 40, 60, 80, 100) at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa

Catalyst	NiW/ Mix0	NiW/ Mix20	NiW/ Mix40	NiW/ Mix60	NiW/ Mix80	NiW/ Mix100
Conversion (wt.%)	63.35	63.13	55.89	54.97	55.10	59.44
Total distilled fuels (wt.%)	52.35	49.50	40.12	42.27	40.40	44.97
Gasoline (wt.%)	11.52	14.67	16.31	13.45	12.48	11.22
Kerosene (wt.%)	5.14	8.46	7.34	7.86	7.95	9.31
Diesel (wt.%)	35.69	26.37	16.47	20.96	19.97	24.44
Gas yield (wt.%)	5.23	7.97	11.10	8.70	10.87	10.80
Gas composition (mol%)						
CH_4	0.01	0.00	0.00	0.00	0.00	0.01
C_2H_4	0.28	1.14	0.17	0.18	0.23	0.20
C_2H_6	42.42	45.41	50.71	54.10	46.37	47.52
C_3H_6	1.91	1.91	1.34	1.69	1.68	2.88
C_3H_8	29.15	30.89	30.15	28.31	32.59	30.73
C_4H_{10}	18.35	20.65	17.63	15.72	19.13	18.66
$C_5^{=}$	7.88	0.00	0.00	0.00	0.00	0.00
Coke yield (wt.%)	5.77	5.66	4.67	4.00	3.83	3.67

3.3.3. Coke analysis

The type of coke deposited onto the NiW/MCM-48-USY composite catalysts was determined by using TGA. Fig. 28 and 29 illustrate profiles of weight loss with temperature of coked NiW/MCM-48-USY and MCM-48-USY composite catalysts, respectively. The coke on the catalyst began to burn off at two temperature ranges 200-300 °C and 450-550 °C. This indicates that there was probably more than one type of coke species on the catalysts, soft and hard coke.

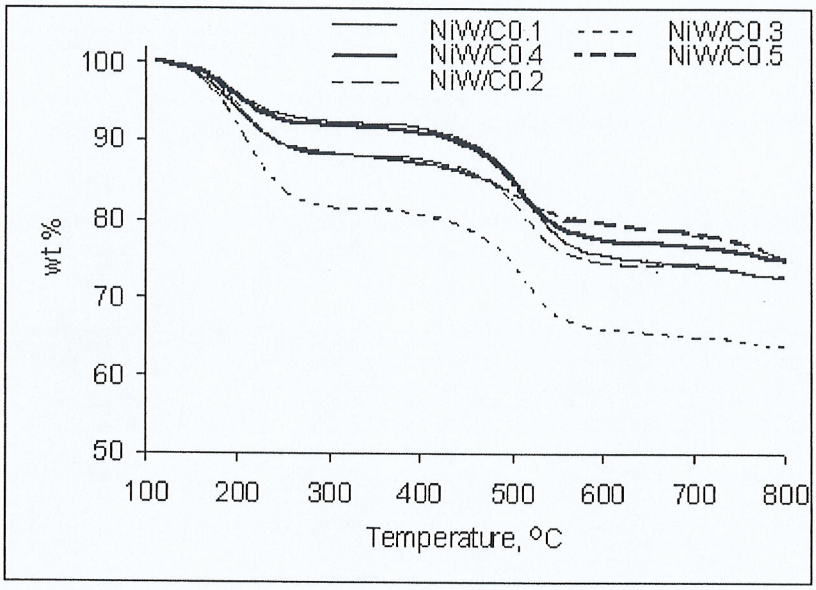

Fig. 28: Profiles of weight loss with temperature of coked NiW/MCM-48-USY with different SiO_2/USY ratios

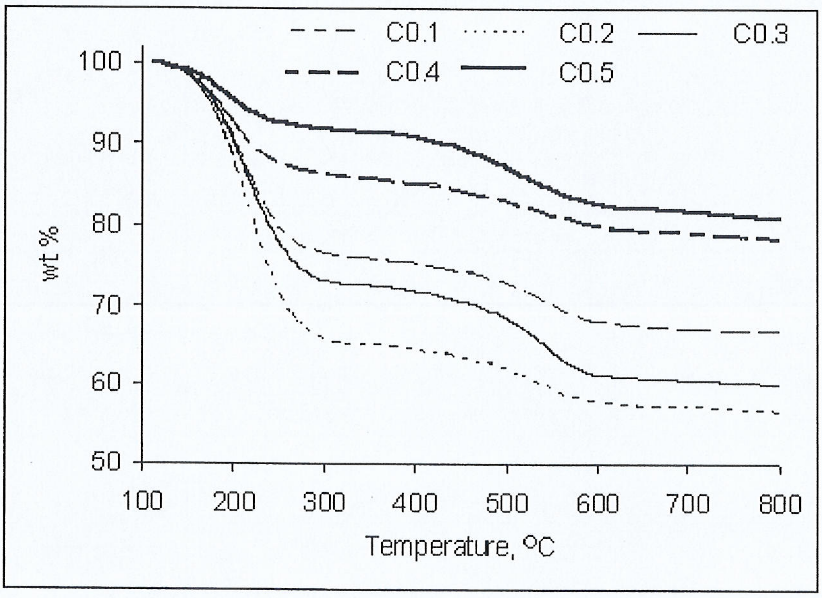

Fig. 29: Profiles of weight loss with temperature of coked MCM-48-USY with different SiO_2/USY ratios

3.4. Modeling of gas oil hydrocracking

Design of experiment (DOE) was used to evaluate the effects of various variables in the hydrocracking of gas oil over NiW/MCM-48 catalyst with SiO_2/Al_2O_3 ratio of 50 (NiW/M50) such as reaction temperature, contact time and catalyst to gas oil ratio. The response surface methodology (RSM) was used to obtain the values of conversion and yields of total distillate fuels, gasoline, kerosene, diesel, gas and coke.

The seven responses designated by the letter "Y ", are:

Y_1 = Conversion, Y_2 = yield of total distillate fuels, Y_3 = Gasoline yield,

Y_4 = kerosene yield, Y_5 = diesel yield, Y_6 = gas yield, Y_7 = coke yield.

The process was studied with a 3^3 full factorial design. The experimental results obtained according to the design given in Table 3.8 are presented in Table 17.

(2) Tables 5.2-5.8 show the results of sequential model sum of squares for conversion and yields of total distillate fuels, gasoline, kerosene, diesel, gas and coke, respectively.

The analyses of variance (ANOVA) for the quadratic model of kerosene, diesel and coke yield (Tables 18-24), the Model F-values of 261.15, 167.43 and 113.58 imply that the models are significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. In kerosene model, A, B, C, A^2, C^2, BC are significant model terms, while in diesel and coke models, A, B, C, A^2, AC and A, B, C, A^2 are significant model terms, respectively.

Table 17: The experimental results obtained based on the 3^3 full factorial design

A: Temperature ^{o}C	B: time min	C: C/O*	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7
440	20	0.02	21.88	13.15	1.86	1.65	9.64	6.40	2.33
440	40	0.02	27.03	17.67	3.29	3.02	11.36	6.86	2.50
440	60	0.02	28.77	18.67	3.86	3.02	11.79	7.37	2.73
440	20	0.04	29.90	19.70	4.12	3.37	12.21	7.10	3.10
440	40	0.04	31.68	21.48	4.56	3.81	13.11	7.10	3.10
440	60	0.04	33.83	22.86	4.82	4.22	13.82	7.83	3.14
440	20	0.06	34.23	23.50	4.88	4.23	14.39	7.60	3.13
440	40	0.06	37.86	26.86	5.84	4.81	16.21	7.83	3.17
440	60	0.06	41.52	29.72	7.51	5.16	17.05	8.53	3.27
460	20	0.02	45.76	34.19	10.55	4.97	18.67	8.30	3.27
460	40	0.02	51.99	39.09	12.94	7.32	18.83	9.23	3.67
460	60	0.02	54.19	40.22	13.80	7.54	18.88	10.20	3.77
460	20	0.04	55.13	42.13	13.83	8.99	19.31	9.00	4.00
460	40	0.04	56.29	42.79	14.27	9.20	19.32	9.50	4.00
460	60	0.04	57.91	42.91	14.72	9.14	19.05	10.67	4.33
460	20	0.06	58.12	43.59	13.98	9.15	20.46	10.20	4.33
460	40	0.06	59.10	44.00	14.18	9.15	20.67	10.67	4.43
460	60	0.06	61.21	44.74	14.41	9.34	20.99	11.87	4.60
480	20	0.02	60.65	44.72	14.11	9.27	21.34	11.37	4.56
480	40	0.02	64.76	47.80	15.30	10.65	21.85	12.33	4.63
480	60	0.02	67.03	49.56	16.10	11.80	21.66	12.80	4.67
480	20	0.04	68.24	51.94	17.53	11.93	22.48	11.63	4.67
480	40	0.04	70.73	53.36	17.72	12.56	23.08	12.57	4.80
480	60	0.04	73.10	55.17	18.30	13.19	23.68	13.03	4.90
480	20	0.06	73.06	56.09	18.47	13.25	24.37	12.10	4.87
480	40	0.06	74.35	56.81	18.61	13.38	24.82	12.57	4.97
480	60	0.06	76.64	58.20	19.22	13.68	25.30	13.27	5.17
460	40	0.04	55.87	42.67	14.00	9.45	19.22	9.23	3.97
460	40	0.04	56.04	43.04	14.34	9.26	19.44	9.00	4.00
460	40	0.04	56.34	42.74	14.25	9.19	19.30	9.60	4.00
460	40	0.04	56.30	42.77	14.26	9.20	19.31	9.70	3.83
460	40	0.04	56.44	42.54	14.18	9.15	19.21	9.83	4.07

* C/O: is the catalyst to gas oil ratio

Table 18: Analyses of variance (ANOVA) for conversion

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F Value	Prob > F	Comment
Model	7312.18	9	812.46	725.45	< 0.0001	significant
A	6492.68	1	6492.68	5797.34	< 0.0001	
B	123.93	1	123.93	110.65	< 0.0001	
C	491.2	1	491.2	438.6	< 0.0001	
A^2	154.14	1	154.14	137.64	< 0.0001	
B^2	0.75	1	0.75	0.67	0.4223	
C^2	4.89	1	4.89	4.37	0.0484	
AB	0.9	1	0.9	0.81	0.3792	
AC	1.56	1	1.56	1.39	0.2512	
BC	4.99	1	4.99	4.46	0.0463	

Table 19: Analyses of variance (ANOVA) for total distillate fuels

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F Value	Prob > F	Comment
Model	4964.38	9	551.6	370.69	< 0.0001	significant
A	4356.8	1	4356.8	2927.94	< 0.0001	
B	60.65	1	60.65	40.76	< 0.0001	
C	341.82	1	341.82	229.72	< 0.0001	
A^2	146.45	1	146.45	98.42	< 0.0001	
B^2	2.23	1	2.23	1.5	0.2342	
C^2	6.75	1	6.75	4.53	0.0447	
AB	1.86	1	1.86	1.25	0.2761	
AC	0.21	1	0.21	0.14	0.7138	
BC	3.98	1	3.98	2.67	0.1162	

Table 20: Analyses of variance (ANOVA) for gasoline yield

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F Value	Prob > F	Comment
Model	848.25	9	94.25	285.5	< 0.0001	significant
A	729.87	1	729.87	2210.95	< 0.0001	
B	9.99	1	9.99	30.26	< 0.0001	
C	35.53	1	35.53	107.64	< 0.0001	
A^2	54.76	1	54.76	165.87	< 0.0001	
B^2	0.079	1	0.079	0.24	0.63	
C^2	2.85	1	2.85	8.65	0.0076	
AB	0.28	1	0.28	0.84	0.3704	
AC	0.21	1	0.21	0.62	0.4386	
BC	0.98	1	0.98	2.97	0.0989	

Table 21: Analyses of variance (ANOVA) for kerosene yield

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F Value	Prob > F	Comment
Model	371.06	9	41.23	261.15	< 0.0001	significant
A	324.45	1	324.45	2055.02	< 0.0001	
B	5.87	1	5.87	37.19	< 0.0001	
C	29.16	1	29.16	184.69	< 0.0001	
A^2	1.49	1	1.49	9.44	0.0056	
B^2	0.67	1	0.67	4.26	0.0511	
C^2	3.76	1	3.76	23.8	< 0.0001	
AB	0.095	1	0.095	0.6	0.4452	
AC	0.36	1	0.36	2.28	0.145	
BC	2.02	1	2.02	12.78	0.0017	

Table 22: Analyses of variance (ANOVA) for diesel yield

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F Value	Prob > F	Comment
Model	512.77	9	56.97	167.43	< 0.0001	significant
A	440.06	1	440.06	1293.21	< 0.0001	
B	4.86	1	4.86	14.27	0.001	
C	50.8	1	50.8	149.3	< 0.0001	
A^2	12.12	1	12.12	35.61	< 0.0001	
B^2	0.15	1	0.15	0.45	0.5089	
C^2	1.06	1	1.06	3.12	0.0912	
AB	1.31	1	1.31	3.86	0.0622	
AC	2.27	1	2.27	6.67	0.017	
BC	0.17	1	0.17	0.51	0.4836	

Table 23: Analyses of variance (ANOVA) for gas yield

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F Value	Prob > F	Comment
Model	125.89	3	41.96	318.76	< 0.0001	significant
A	112.75	1	112.75	856.46	< 0.0001	
B	7.83	1	7.83	59.46	< 0.0001	
C	5.31	1	5.31	40.36	< 0.0001	

Table 24: Analyses of variance (ANOVA) for coke yield

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F Value	Prob > F	Comment
Model	18.09	9	2.01	113.58	< 0.0001	significant
A	15.62	1	15.62	882.84	< 0.0001	
B	0.3	1	0.3	16.9	0.0005	
C	1.88	1	1.88	105.97	< 0.0001	
A^2	0.14	1	0.14	7.84	0.0104	
B^2	0.017	1	0.017	0.97	0.3349	
C^2	0.045	1	0.045	2.54	0.1251	
AB	3.00E-04	1	3.00E-04	0.017	0.8976	
AC	0.062	1	0.062	3.48	0.0754	
BC	7.50E-03	1	7.50E-03	0.42	0.5218	

The quadratic models for conversion, yields of total distillate fuels, gasoline, kerosene, diesel and coke are shown in Equations 1-5 and 7 respectively, while the linear model for gas yield is shown in Equation 6. These model equations are applicable in the range of variables studied.

$$\text{Conversion} = 56.26 + 18.99\,A + 2.62\,B + 5.22\,C - 4.64\,A^2 - 0.32\,B^2 - 0.83\,C^2 - 0.27\,AB - 0.36\,AC - 0.65\,BC \quad (1)$$

$$\text{Yield of total distillate fuels} = 42.61 + 15.56\,A + 1.84B + 4.36C - 4.52A^2 - 0.56B^2 - 0.97\,C^2 - 0.39\,AB - 0.13\,AC - 0.58\,BC \quad (2)$$

$$\text{Gasoline Yield} = 14.15 + 6.37\,A + 0.74\,B + 1.40\,C - 2.77\,A^2 - 0.10\,B^2 - 0.63\,C^2 - 0.15\,AB + 0.13\,AC - 0.29\,BC \quad (3)$$

$$\text{Kerosene Yield} = 9.09 + 4.25\,A + 0.57\,B + 1.27\,C - 0.46\,A^2 - 0.31\,B^2 - 0.72\,C^2 + 0.089\,AB + 0.17\,AC - 0.41\,BC \quad (4)$$

$$\text{Diesel Yield} = 19.37 + 4.94\,A + 0.52\,B + 1.68\,C - 1.30\,A^2 - 0.15\,B^2 + 0.39\,C^2 - 0.33\,AB - 0.44\,AC + 0.12\,BC \quad (5)$$

$$\text{Gas Yield} = 9.85 + 2.50\,A + 0.66\,B + 0.54\,C \quad (6)$$

$$\text{Coke Yield} = 4.03 + 0.93\,A + 0.13\,B + 0.32\,C - 0.14\,A^2 + 0.049\,B^2 - 0.079\,C^2 + 0.005\,AB - 0.072\,AC - 0.025\,BC \quad (7)$$

where A , B and C are reaction temperature, contact time and catalyst to gas oil ratio in terms of coded factor, respectively.

The region in the important factors (reaction temperature, contact time and catalyst to gas oil ratio) that leads to the best possible response (low coke yield and high conversion, yields of total distillate fuels, gasoline, kerosene, diesel and gas) was determined using statistical design of experiment (DOE) software. It was found that the optimum operating conditions for hydrocracking of gas oil over NiW/MCM-48 catalyst with SiO_2/Al_2O_3 ratio of 50 (NiW/M50) are:

(1) reaction temperature of 465 °C

(2) contact time of 30 min

(3) catalyst to gas oil ratio of 0.05.

4. Conclusions

The performance of USY zeolite for hydrocracking of gas oil was investigated at reaction temperature of 450 °C, 90 min contact time, 0.04 catalyst to gas oil ratio and 1000 kPa hydrogen pressure. The maximum values of total conversion and yield of total distillate fuels were 63.35 and 52.35 wt%, respectively, compared to 47.81 and 36.58 wt% over unloaded USY zeolite. A series of NiW/USY catalysts with different nickel (NiO = 0-10.4 wt %) and tungsten (WO_3 = 0-30 wt %) loadings were prepared. It was found that the optimum contents of tungsten and nickel were 23 and 5 wt%, respectively and maximum values of total conversion, yield of total distillate fuels, gasoline, kerosene, diesel gas and coke were 63.35, 52.35, 11.52, 5.14, 35.69, 5.23 and 5.77 wt%, respectively. Mesoporous MCM-48 materials with different SiO_2/Al_2O_3 ratios were synthesized by hydrothermal method. The results revealed the formation of MCM-48 material contains mesopore size in range of 3.23-4.68 nm. It has been shown that these materials provided a large surface area, improved mass transfer and relatively strong acidity, which resulted in high hydrocracking activity. Among prepared NiW/MCM-48 with different SiO_2/Al_2O_3 ratios (5, 25, 50, 75, 125) catalysts, NiW/MCM-48 with SiO_2/Al_2O_3 of 50 (NiW/M50) exhibited better catalytic activity for gas oil hydrocracking. Composite materials containing microporous USY coated with mesoporous MCM-48 were successfully synthesized. The pore size and the acidity effects of NiW/MCM-48-USY composite catalysts with different meso/microporous ratios (SiO_2/USY ratios of 0.1, 0.2, 0.3, 0.4, 0.5) on the hydrocracking activity were investigated for gas oil hydrocracking. It has been shown that these materials provided a large surface area, improved mass transfer and relatively strong acidity, which resulted in high hydrocracking activity. The amounts of gasoline, kerosene, and diesel increased with the SiO_2/USY ratio for all catalysts, while the amounts of coke decreased. DOE was used to evaluate the effects of temperature, contact time and catalyst to gas oil ratio on the total conversion and yields of total distillate fuels, gasoline, kerosene, diesel, gas and coke and to obtain the optimum operating conditions for hydrocracking of gas oil. It was found that the optimum operating conditions for hydrocracking of gas oil over prepared NiW/MCM-48 catalyst with SiO_2/Al_2O_3 ratio of 50 (NiW/M50) are: reaction temperature of 465 °C, contact time of 30 min and catalyst to gas oil ratio of 0.05.

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Appendix B

Publication in National & Peer-Reviewed International Journals

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Hydrocracking of petroleum gas oil over NiW/MCM-48-USY composite catalyst

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Abstract

MCM-48-USY composite materials were prepared by coating USY zeolite by a layer of MCM-48 mesoporous material at different meso/microporous ratios (SiO$_2$/USY ratios of 0.1, 0.2, 0.3, 0.4, 0.5) and used as support for nickel and tungsten. The NiW/MCM-48-USY catalysts were prepared using the incipient wetness method. The prepared catalysts were characterized by TPD-TGA acidity, TGA thermal stability, BET surface area, pore volume, pore size, XRD, SEM and TEM and then tested for hydrocracking of petroleum gas oil at reaction temperature of 450 °C, contact time of 90 min and catalyst to gas oil ratio of 0.04. In all prepared samples, the catalyst activity and properties were improved with increasing SiO$_2$/USY ratio and found that maximum values of a total conversion and liquid product (total distillate fuels) were obtained at SiO$_2$/USY ratio of 0.5. Finally, the obtained results from hydrocracking of gas oil over composite MCM-48-USY catalysts were compared with those obtained over physically mixed USY and MCM-48 catalysts.

Keywords: Petroleum gas oil; NiW/MCM-48-USY composite catalyst; A high-pressure shaking reactor

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1. Introduction

The ever increasing demand for lighter engine fuel and higher price of light crude oil have stimulated the petroleum refining industry into looking for the possibility of processing heavy fractions as well as the comparatively cheaper heavy crude oils. Therefore, to meet the growing demand for lighter fuel the need for more efficient process. In petroleum refining, hydrocracking of heavy hydrocarbons has been carried out. Among the technologies, solid catalyzed hydrocracking processes are believed to be a promising technology, because of its high product quality to produce high quality gasoline, kerosene and diesel [1].

Most of the conventional hydrocracking catalysts are dual functional catalysts. They have a hydrogenation–dehydrogenation function as well as an acidic function. The cracking activity is controlled mainly by the support that is acidic in nature, whereas the hydrogenation–dehydrogenation catalyst activity is due to the metals loaded on the support. High acidity tends to cause coking, which leads to deactivation. In order to prepare a suitable hydrocracking catalyst, a good balance between the two functions has to be maintained. The selection of a proper catalyst for a given high activity is a complex problem. While microporous zeolites such as Y, ZSM-5 and β are playing important roles in modern petrochemical industry for their abundant uniform microporous structures and strong intrinsic acidities, much attention is being given to the development of mesoporous zeolites that provide larger pores (>2 nm) to allow the conversion of large molecules and thus overcome the limitations of microporous zeolites. At present, a popular resolvent is to prepare a composite zeolites material comprising of both the microporous zeolites matrix and mesoporous material by multi-step crystallization. However, all of these methods mainly aim at modifying mesoporous material on its structure stability and acidity, whose level of standard are still far away from microporous zeolites [2]. One of these mesoporous zeolites that have aroused many research interests is the so called MCM-41 [2–7]. Despite the intensive research on synthesis, characterization and application of MCM-41 materials, MCM-48, being the cubic member of the M41S

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family, has received much less attention especially in the field of catalysis. A contraction of the unit cell occurred by substituting the silicon with larger aluminum atoms. The mesoporous molecular sieves MCM-48 possesses bi-continuous and three dimensional pore channels. Consequently, both the diffusional limitation and the pore blockage are reduced as compared to MCM-41. These characteristic properties show its potential applications in catalysis, adsorption and separation [8].

The main goal of this work is to develop zeolite-based catalysts with proper mesoporosity that are favorable for the hydrocracking of heavy oils. For this purpose, the NiW/MCM-48-USY composite catalysts with different SiO_2/USY ratios were prepared, characterized and tested for hydrocracking of petroleum gas oil.

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 [9]. 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

The MCM-48 /USY composite materials were prepared by coating USY zeolite by a layer of MCM-48 mesoporous material. The preparation procedure was done according to the procedure reported previously [6,10] with some modifications. About 3.00 g of N-hexadecyltrimethylammonium bromide (HDTMAB) was mixed with different amounts of USY zeolite (to give SiO_2/USY weight ratio in the range of 0.1–0.5) and 7 g distilled water. Hexadecyltrimethylammonium (HDTMA) ion-exchanged USY was titrated with 33 wt.% solution of NaOH to pH = 11 and added to the freshly prepared MCM-48 gel. The initial precursor of solution used for the preparation of MCM-48 mesophase had the following chemical composition: 1.0TEOS: $10.6NH_3$: 46.7EtOH: 0.44HDTAMB: $423H_2O$. About 3.24 of HDTMAB was dissolved in 152 ml distilled water and 45.22 g ethanol, and then 12.87 g of aqueous ammonia (28 wt.%) was added to the surfactant solution. The formed solution was stirred and then 4.25 g of TEOS and 0.04 g of aluminium isopropoxide (to give SiO_2/Al_2O_3 molar ratio of 125) were added. The gel was stirred vigorously and then transferred into the Teflon bottle and aged for 24 h at 110 °C. The samples were filtered, washed with distilled water and dried at ambient temperature followed calcinations at 550 °C for 6 h in a muffle furnace. The resultant material (in Na-form) was converted to H-form by ion-exchanging with 4 M NH_4Cl aqueous solution with liquid/solid ratio of 20 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 room temperature and then calcined at 500 °C for 3 h.

The composite MCM-48/USY materials were coded as C(Y) where C referred to composite MCM-48/USY and Y referred to SiO_2/USY weight ratio.

Synthesized NiW catalysts were prepared by impregnation of the composite MCM-48/USY with aqueous solution of NiW precursors $[(NH_4)_{10}(W_{12}O_{41})$ and $Ni(NO_3)_2$·$6H_2O]$ 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 [11,12]. The composition of the catalyst was 23 wt.% of WO_3 and 5.2 wt.% of NiO. 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 settled 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 [13,14].

2.3. Characterization of catalysts

The apparatus and methods employed in characterization of catalysts were already described [9]. Pore volume, surface area and average pore diameter of synthesized catalysts were measured using Accelerated Surface Area and Porosimetry System (ASAP 2000) supplied by Micromeritics, USA. The samples were dried overnight at temperature of 105 °C and degassed for 12 h under vacuum at temperature of 300 °C using ASAP2000 instrument before measurements were performed [15].

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. 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 1 h (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 type of surface acidity corresponded to the temperature peaks. Weak acidity sites associated with the Lewis acid type occurred in the low temperature region of around 100–300 °C whereas strong acid sites associated with the Bronsted acid type occurred in the high temperature region of around 400–500 °C. From these results it was possible to quantitatively identify the number of strong and weak acid sites in the sample. The acidity was calculated by the following formula and reported in units of millimoles of acid sites per gram of catalyst.

$$\text{Acidity} = \frac{W\left(\frac{1}{\text{Mb}}\right)\left(\frac{1000\text{mg}}{1\text{g}}\right)}{W_z} \tag{1}$$

where W is the mass loss due to the desorption of base in the temperature of interest (g), W_Z is 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.

Powder X-ray diffraction (XRD) patterns of calcined mesoporous aluminosilicate (MCM-48) were obtained using Siemens D5000 X-ray diffractometer with CuKα radiation ($\lambda = 1.54056$ Å) at 40 kV and 30 mA and scanning speed of 2°/min.

TEM images were carried out using Philips (CM12) transmission electron microscope equipped with Image Analyzer and operated at 80 kV. Samples were crushed and mixed with acetone in glass vials and shaken vigorously for few minutes and then kept for about 3 min to allow coarser particles to settle down and applied a drop of solution on a carbon film coated 400 mesh grid.

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.

2.4. Reactor set-up and procedure

The reactor set-up and procedure used in this work were already described [9]. Initially desulphurized petroleum gas oil (DS-GO) (30 g) 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 conversion, product yield, and catalyst to gas oil ratio were obtained using the following equations:

$$\%Conversion = \frac{(W_{\mathrm{GO}} - W_{\mathrm{R}})}{W_{\mathrm{GO}}} \times 100 \tag{2}$$

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

$$Y_I = \frac{W_I}{W_{\mathrm{GO}}} \times 100 \tag{3}$$

where Y_{I} is the yield of the product (wt.%), I is the distillate fraction (gasoline, kerosene, diesel), W_{I} is weight of the distillate fraction.

$$\text{Catalyst to gas oil ratio} = \frac{W_{\mathrm{CA}}}{W_{\mathrm{GO}}} \tag{4}$$

where W_{CA} is weight of catalyst loaded.

2.5. 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 [9]. The distillation curve of 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 [5,16].

2.6. Gas analysis

The product gases were analyzed using a gas chromatograph (FID) (Hewlett Packard, model No. 5890 series II) equipped with Porapak Q, 270 cm-length × 3.15 mm stainless steel column (Supelco).

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 presents X-ray diffraction (XRD) traces of the samples prepared by coating USY zeolite by a layer of MCM-48 mesoporous material. XRD analysis shows one new peak at 2θ value of 2 in the addition of the USY pattern which did not change from the original pattern. The position of this new peak was in mesophase range (2θ value of 2) which confirmed that the mesophase species are present in all prepared composite materials [2,17]. The peak intensity is increased with increasing SiO_2/USY ratio due to increase MCM-48 in the prepared composite.

The surface characteristics and porosity in terms of BET surface area, pore volume and average pore diameter of the prepared composite catalysts are given in Table 1. The surface area, average pore diameter and pore volume values obtained are of the catalysts containing USY zeolites and mesoporous MCM-48 material and thus represent the properties of the composite supports. The catalysts loaded with NiW showed lower surface area and pore volume compared to unloaded supports. This is reasonable as the impregnated metals both fill up and plug some of pores, making less area available for nitrogen adsorption, and contribute to the weight of the catalyst, lowering the surface area and pore volume measured on a weight basis. Similarly, catalysts prepared with higher SiO_2/USY ratio showed lower surface area and pore volume as compared to those having lower SiO_2/USY ratios. This is due to decrease amount of USY zeolites in prepared composite which is having higher surface area and pore volume than MCM-48.

Table 1
The surface characteristics of the prepared composite materials

Catalyst	Surface area, m^2/g	Mesoporous area, %	Microporous area, %	Pore volume, cm^3/g	Average pore size (APS), nm
C0.1	689.95	17.93	82.07	0.3738	2.167
C0.2	596.35	18.82	81.18	0.3261	2.187
C0.3	586.41	51.01	48.99	0.3228	2.202
C0.4	537.7	69.69	30.31	0.3048	2.267
C0.5	494.12	87.83	12.17	0.2837	2.297
NiW/C0.1	433.5	32.81	67.19	0.2683	2.476
NiW/C0.2	356.77	62.92	37.08	0.2364	2.560
NiW/C0.3	299.17	77.12	22.88	0.2041	2.729
NiW/C0.4	287.14	85.41	14.59	0.1972	2.747
NiW/C0.5	228.66	89.23	10.77	0.1589	2.780

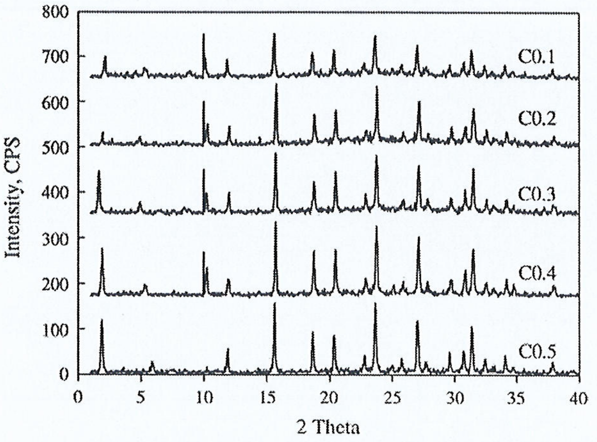

Fig. 1. XRD pattern for composite MCM-48/USY materials with different SiO_2/USY ratios.

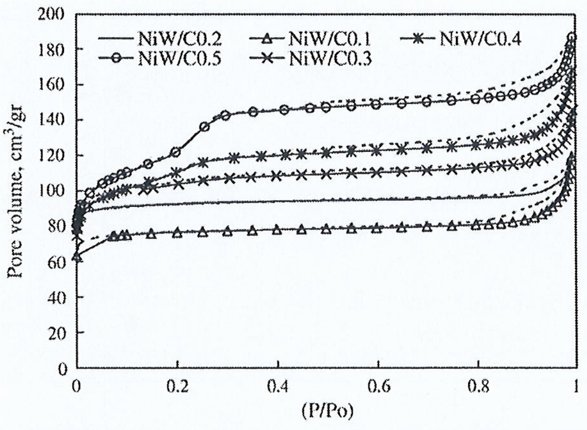

Fig. 2. Adsorption (solid line) and desorption (dotted line) isotherm of NiW catalysts supported on MCM-48/USY with different SiO_2/USY ratios.

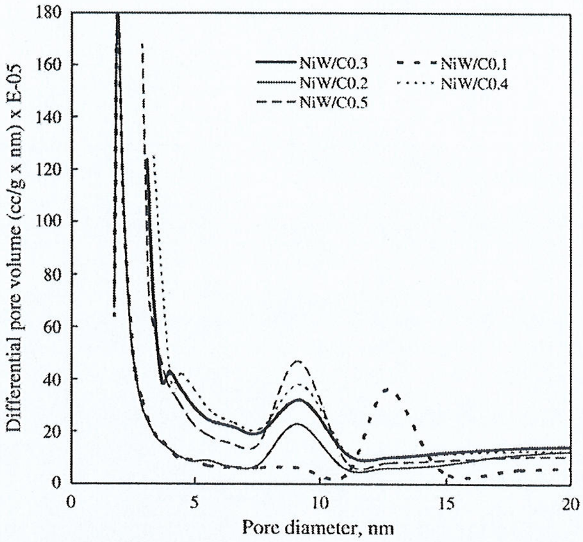

Fig. 3. Pore size distribution of NiW catalysts supported on MCM-48/USY with different SiO_2/USY ratios.

Fig. 2 shows the N_2 adsorption–desorption isotherms of NiW supported on MCM-48/USY composite catalysts obtained from N_2 adsorption. It is seen that adsorption capacity is increased with increase SiO_2/USY ratio. According to the IUPAC definition, mesoporous materials exhibit a type IV adsorption–desorption isotherm [18]. Depending on the pore size, a sharp increase is seen at relative pressures from 0.25 to 0.5. This corresponds to capillary condensation of N_2 in the mesopores. The pore size distributions of composite catalysts are illustrated in Fig. 3. As shown, all catalysts exhibit two main pore size peaks occur centered at 2 and 15 nm. The peak size in mesoporous range is enlarged with increase SiO_2/USY ratio due to increase amount of mesophase (MCM-48) in prepared materials.

Surface acidity is one of the unique properties of catalysts responsible for hydrocracking processes. Generally, in zeolites both Brönsted and acid Lewis sites exist simultaneously. Isopopylamine was used as basic probe molecules to react with bridging hydroxyl groups giving rise to the surface acidity. The type of surface acidity corresponded to the temperature peaks. Weak acidity sites associated with the Lewis acid type occurred in the low temperature region of around 100–300 °C whereas strong acid sites associated with the Bronsted acid type

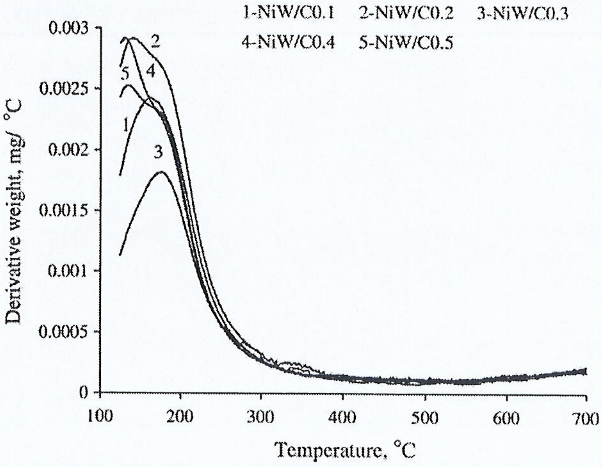

Fig. 4. TGA-TPD acidity types of NiW supported on MCM-48-USY composite catalysts.

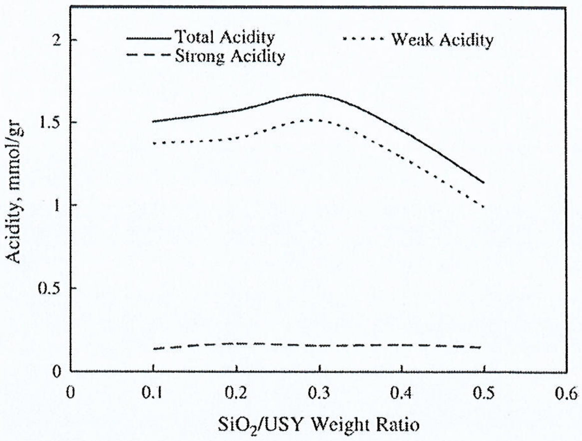

Fig. 5. TGA-TPD acidity for NiW/MCM-48-USY composite catalysts.

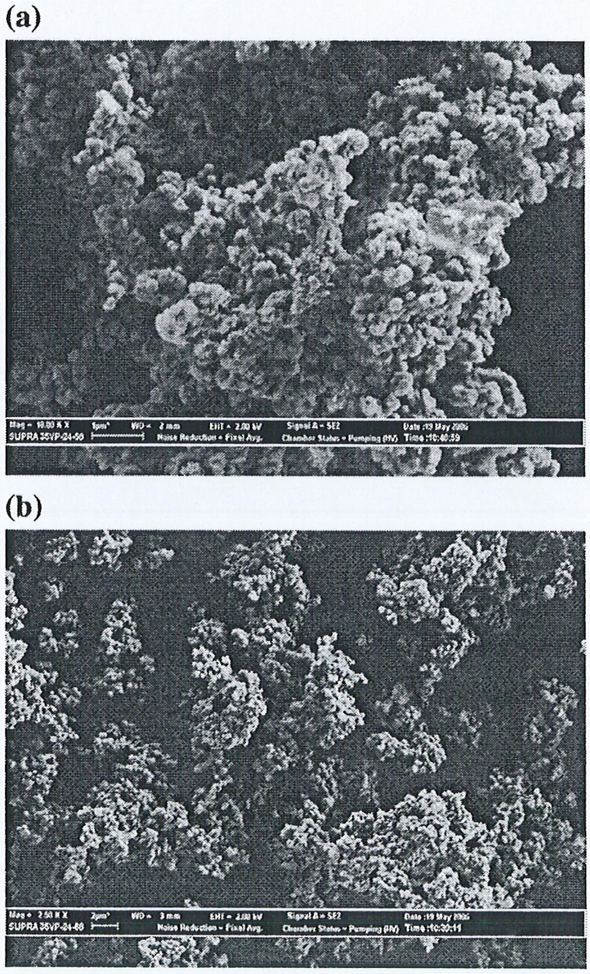

Fig. 6. Scanning electron micrographs of: (a) C0.5 support, (b) NiW/C0.5 catalyst.

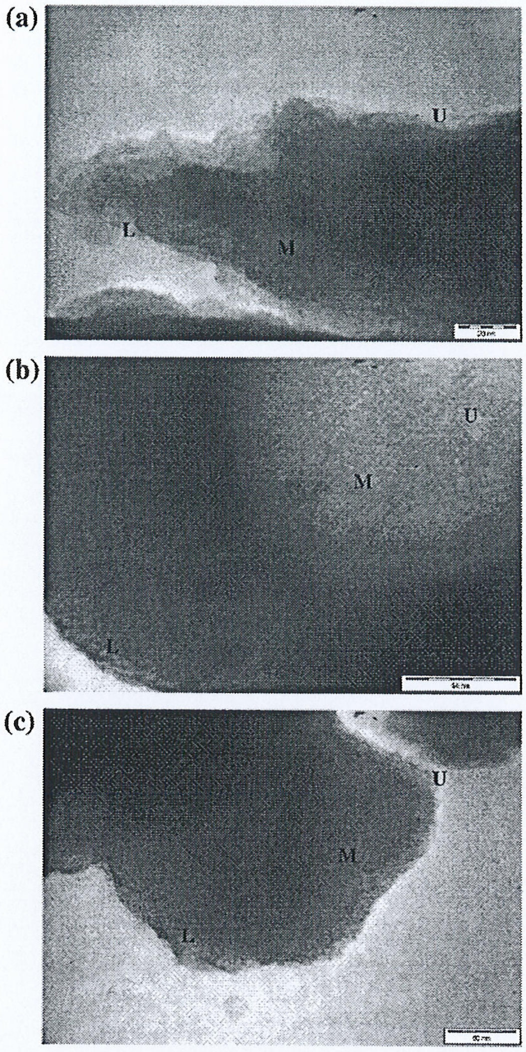

Fig. 7. TEM images of NiW/MCM-48-USY with different SiO_2/USY ratios: (a) SiO_2/USY=0.2, SiO_2/USY=0.4, SiO_2/USY=0.5.

occurred in the high temperature region of around 400–500 °C. The temperature programmed desorption (TPD) using TGA of NiW/MCM-48-USY composite catalysts with different SiO_2/USY ratios (NiW/C0.1-C0.5) are presented in Fig. 4. For all catalysts, the major peaks were found at 200–300 °C. This range has been assumed to be the large amount of weak acid sites (Lewis type). Fig. 5 presents amounts of weak and strong acid sites of NiW/MCM-48-USY composite catalysts as a function of SiO_2/USY ratio. In contrast to the SiO_2/USY ratio, all catalysts show similar amount of strong acid sites (Bronsted) and there are no significant differences between all catalysts were observed. Total and weak acid sites were increased with decreasing SiO_2/USY ratio due to the increment of USY zeolites concentration in the composite materials.

Scanning electron microscopy images (SEM) of C0.5 and NiW/C0.5 composite catalyst are shown in Fig. 6a and b, respectively. SEM was carried out in order to observe the changes in the morphology and surface texture of coated materials. The SEM images of composite material show that there was an overgrowth of non-uniform cabbage-like crystals on USY zeolites. The SEM micrograph of unloaded materials indicated smooth and almost uniform particles.

The transmission electron microscopy (TEM) images of NiW/MCM-48-USY composite catalysts with different SiO_2/USY ratios are shown in Figs. 7 and 8. The TEM image shows a highly ordered pore arrangement in middle regions (region M on Fig. 7a, b, c). However, the pores are orientated at different angles in different areas. For example, in upper region (region U on Fig. 7a, b, c) the pores are oriented at an angle to the plane of the image whereas in lower region (region L on Fig. 7a, b, c) they are oriented parallel to the image. The composite catalysts are composed of a uniform array of pores which are curved at the centre of the image. TEM examination of the synthesized material showed that MCM-48 (light colour) was indeed situated on the outer surface of USY crystals (dark colour) (Fig. 8a, b, c). The coating layer (light colour) was increased with increasing SiO_2/USY ratio (increased from Fig. 8a to c) due to the present higher amount of MCM-48 in the composite.

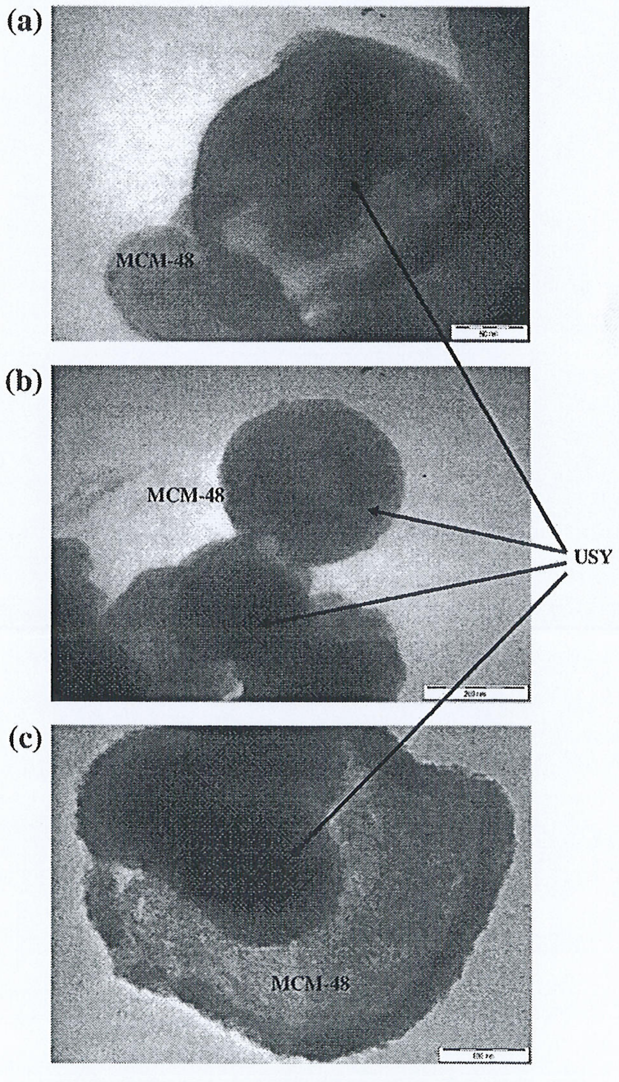

Fig. 8. TEM micrograph of MCM-48 coated USY with different SiO_2/USY ratios: (a) SiO_2/USY=0.2, SiO_2/USY=0.4, SiO_2/USY=0.5.

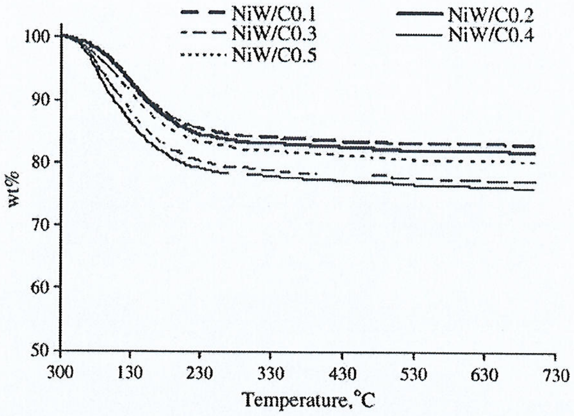

Fig. 9. TGA thermal stability results for NiW/MCM-48-USY composite catalysts with different SiO_2/USY ratios.

Beside this, some of the MCM-48 is present as an independent phase which surrounds the USY crystals. The USY crystals are coated with a layer of MCM-48 a few nanometres thick. Some pieces are covered by a thick layer of MCM-48 and other parts with less thicker layer. The TEM images indicate that MCM-48 layer consists of channels which are parallel to the USY surface without any ordering [10].

The results of thermogravimetric analysis (TGA) of NiW/MCM-48/USY are shown in Fig. 9. Furthermore, all samples showed similar results in TGA analysis. Two steps can be observed in this Figure. The first step, centered at temperature of 110 °C, is associated with physically adsorbed water, constituting about 15% weight loss. The second step in the ATG curve attributed to the main species of the composite materials. These results confirmed that synthesized catalysts posses very high the thermal stability.

3.2. Catalysts performance evaluation

The performance of prepared NiW/MCM-48-USY composite catalysts were evaluated in hydrocracking of petroleum gas oil at reaction temperature of 450 °C, contact time of 90 min and catalyst to gas oil ratio of 0.04. These operating conditions were chosen according to preliminary study carried out in our laboratory at wide range of parameters. The analyses of the gas oil feed are given in Tables 2 and 3 [9]. The hydrocracking products of petroleum gas oil were analyzed for boiling range distribution. The results presented in Tables 4 and 5 indicate a marked degree of conversion of gas oil feed into gasoline, kerosene, and diesel. The hydrocracking activity of all catalysts was found to increase with SiO_2/USY ratio. The amounts of gasoline, kerosene, and diesel increased with the SiO_2/USY ratio for all catalysts, while the amounts of coke decreased. This is attributed to the good balance between acidity of USY zeolites and high pore size of MCM-48. Another possible reason of higher activity might be less coke deposition on the catalysts. The amount of coke deposition on catalysts with higher SiO_2/USY ratio was less compared to that of low SiO_2/USY ratio. The less coking was probably due to the lower acidity of catalysts with higher SiO_2/USY ratio. Hence, the catalyst surface remained clean and active for further reactions. The hydrocracking activities of unloaded catalysts were found lower than those of NiW-based catalysts. This indicates that the higher hydrogenation activity was achieved by the action of NiW metals. The presence of NiW metals provides sufficient amounts of reactive hydrogen and instantaneously hydrogenates the cracking intermediates produced by the cracking reaction and prevents further cracking to produce lower hydrocarbons. The active component (W) is responsible for the principal chemical reaction, saturate aromatics in the feed, saturate olefins formed in the cracking, and protects the catalyst from poisoning by the coke. The role of the promoter (Ni) is to increase the number of sulphur vacancies and to modify the acid–base properties of the catalyst. The presence of promoter

Table 2
Distillation analysis of the gas oil [9]

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 **

* IBP is initial boiling point.
** FBP is final boiling point.

Table 3
Elemental composition analysis, wt.% of the gas oil [9]

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

Table 4
Gas oil hydrocracking over MCM-48-USY composite catalysts with different SiO_2/USY ratios

Catalyst	C0.1	C0.2	C0.3	C0.4	C0.5
Conversion (wt.%)	52.41	55.20	60.92	62.82	65.69
Total distilled fuels (wt.%)	36.41	38.53	44.62	47.19	50.92
Gasoline (wt.%)	10.54	10.64	11.19	14.95	14.40
Kerosene (wt.%)	6.13	5.78	23.70	17.74	18.99
Diesel (wt.%)	19.74	22.11	9.73	14.50	17.53
Gas yield (wt.%)	10.00	11.00	11.30	10.90	10.43
Gas composition (mol%)					
CH_4	0.00	0.00	0.00	0.00	0.00
C_2H_4	0.27	0.22	0.19	0.22	0.20
C_2H_6	37.61	52.04	43.05	50.31	54.20
C_3H_6	2.18	1.46	1.55	1.52	1.29
C_3H_8	34.99	29.92	33.90	29.78	29.11
C_4H_{10}	24.95	16.36	21.31	18.17	15.20
$C_5^=$	0.00	0.00	0.00	0.00	0.00
Coke yield (wt.%)	6.00	5.67	5.00	4.73	4.34

Table 5
Gas oil hydrocracking over NiW/MCM-48-USY composite catalysts with different SiO_2/USY ratios

Catalyst	NiW/ C0.1	NiW/ C0.2	NiW/ C0.3	NiW/ C0.4	NiW/ C0.5
Conversion (wt.%)	57.64	64.49	66.96	68.03	69.74
Total distilled fuels (wt.%)	40.97	48.16	50.32	53.19	56.07
Gasoline (wt.%)	11.58	12.89	13.72	14.47	13.79
Kerosene (wt.%)	6.16	8.77	5.81	8.69	12.97
Diesel (wt.%)	23.23	26.50	30.79	30.03	29.31
Gas yield (wt.%)	10.34	10.06	10.44	10.57	10.03
Gas composition (mol%)					
CH_4	0.00	0.00	0.00	0.00	0.00
C_2H_4	0.33	0.19	0.18	0.17	0.17
C_2H_6	47.65	48.45	36.56	42.93	45.31
C_3H_6	1.63	1.62	1.84	2.58	1.37
C_3H_8	30.41	29.63	35.17	30.56	33.4
C_4H_{10}	19.98	19.91	26.25	20.95	19.75
$C_5^=$	0.00	0.00	0.00	2.81	0.00
Coke yield (wt.%)	6.33	6.27	6.20	4.27	3.64

also enhances the production of sulphur anions, thus leading to more numerous of active sites in the reductive atmospheric of the hydrocracking processes [19]. Generally, for all the catalysts, the gas production was found to be constant. Among the gas product components, the C_2H_6 was found to be in highest quantity followed by C_3H_8 and C_4H_{10}.

It is interesting to compare hydrocracking activity of NiW/MCM-48-USY composite catalysts with that of physically mixed USY and MCM-48 catalysts at different mixing weight percentages (Mix=0, 20, 40, 60, 80, 100). Table 6 shows total conversion and yield of products obtained over NiW/Mix catalyst at the same operating conditions. The NiW/MCM-48-USY composite catalysts show much higher conversion than the mechanical mixture. It can also be seen that NiW/MCM-48-USY is more selective to the light products than NiW/Mix. These results would be attributed to the introduction into the composite mesopore walls of the secondary building unit characteristic of USY zeolites which gives rise to the higher hydrothermal stability and more strong acid sites. Beside, the higher activity of NiW/MCM-48-USY composite catalysts might be caused by the faster diffusions of reactant in composite than in mechanical mixture because the composite can provide more interconnected pores and its acid sites are more accessible [4].

Table 6
Gas oil hydrocracking over physically mixed NiW/Mix catalysts with different MCM-48/(MCM-48+USY) percentages (Mix=0, 20, 40, 60, 80, 100)

Catalyst	NiW/ Mix0	NiW/ Mix20	NiW/ Mix40	NiW/ Mix60	NiW/ Mix80	NiW/ Mix100
Conversion (wt.%)	63.35	63.13	55.89	54.97	55.10	59.44
Total distilled fuels (wt.%)	52.35	49.50	40.12	42.27	40.40	44.97
Gasoline (wt.%)	11.52	14.67	16.31	13.45	12.48	11.22
Kerosene (wt.%)	5.14	8.46	7.34	7.86	7.95	9.31
Diesel (wt.%)	35.69	26.37	16.47	20.96	19.97	24.44
Gas yield (wt.%)	5.23	7.97	11.10	8.70	10.87	10.80
Gas composition (mol%)						
CH_4	0.01	0.00	0.00	0.00	0.00	0.01
C_2H_4	0.28	1.14	0.17	0.18	0.23	0.20
C_2H_6	42.42	45.41	50.71	54.10	46.37	47.52
C_3H_6	1.91	1.91	1.34	1.69	1.68	2.88
C_3H_8	29.15	30.89	30.15	28.31	32.59	30.73
C_4H_{10}	18.35	20.65	17.63	15.72	19.13	18.66
$C_5^=$	7.88	0.00	0.00	0.00	0.00	0.00
Coke yield (wt.%)	5.77	5.66	4.67	4.00	3.83	3.67

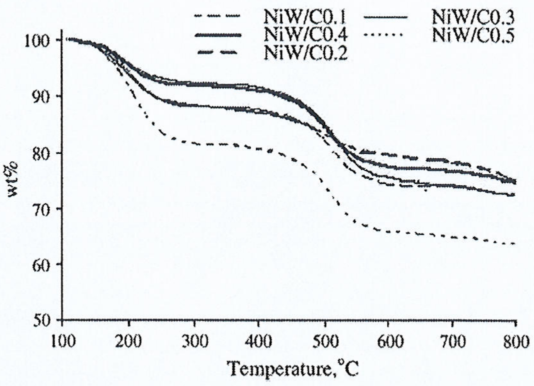

Fig. 10. Profiles of weight loss with temperature of coked NiW/MCM-48-USY with different SiO_2/USY ratios.

3.3. Coke analysis

The type of coke deposited onto the NiW/MCM-48-USY composite catalysts was determined by using TGA. Fig. 10 illustrates profiles of weight loss with temperature of coked NiW/MCM-48-USY composite catalysts. The coke on the catalyst began to burn off at two temperature ranges 200–300 °C and 450–550 °C. This indicates that there was probably more than one type of coke species on the catalysts, soft and hard coke. This is in agreement with literature in which both paraffinic and aromatic coke deposited on the catalyst during heavy oil hydrocracking have been reported [20].

4. Conclusions

The pore size and the acidity effects of NiW/MCM-48-USY composite catalysts with different meso/microporous ratios (SiO_2/USY ratios of 0.1, 0.2, 0.3, 0.4, 0.5) on the hydrocracking activity were investigated via the gas oil hydrocracking reaction. The results showed differences in activity, which is correlated to acid sites and porosity. It has been shown that these materials provided a large surface area, improved mass transfer and relatively strong acidity, which resulted in high catalytic hydrocracking activity. The amounts of gasoline, kerosene, and diesel increased with the SiO_2/USY ratio for all catalysts, while the amounts of coke decreased. This is attributed to the good balance between acidity of USY zeolites and high pore size of MCM-48. The NiW/MCM-48-USY composite catalysts also show much higher hydrocracking activity than the physically mixed USY and MCM-48 catalysts.

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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:

$$\%\text{Conversion} = \frac{W_{\text{GO}} - W_{\text{R}}}{W_{\text{GO}}} \times 100 \tag{1}$$

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

$$Y_I = \frac{W_I}{W_{\text{GO}}} \times 100 \tag{2}$$

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.

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

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

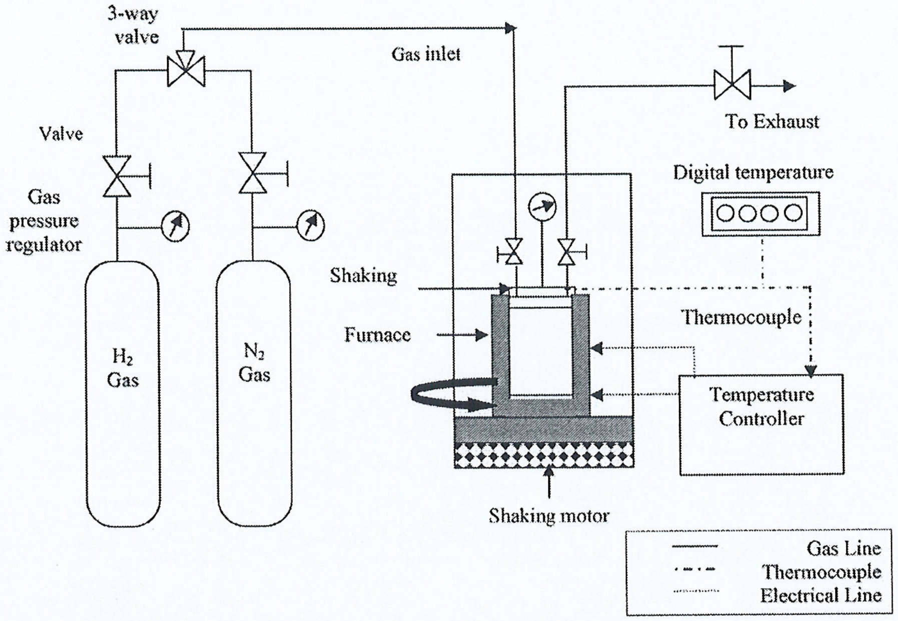

Fig. 1. Schematic diagram of the experimental set-up for hydrocracking of petroleum gas oil.

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:

$$\text{Acidity} = \frac{W(1/\text{Mb})(1000\,\text{mg}/1\,\text{g})}{W_z} \tag{4}$$

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.

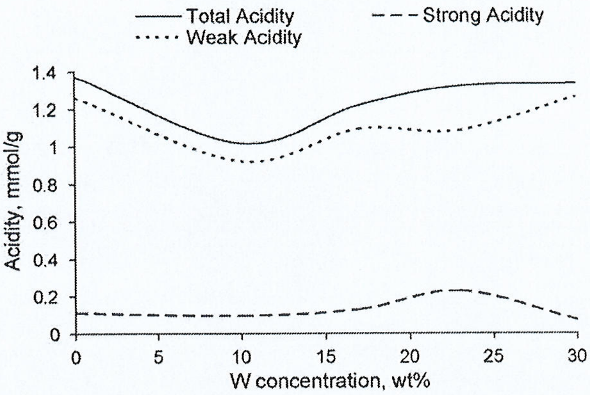

Fig. 2. TGA-TPD acidity vs. tungsten content.

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.

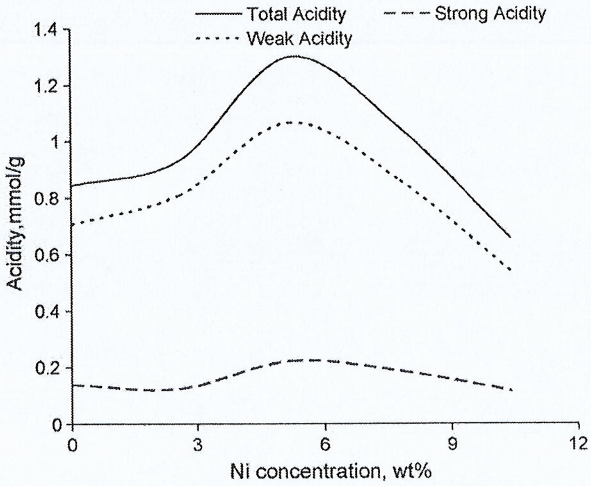

Fig. 3. TGA-TPD acidity vs. nickel content.

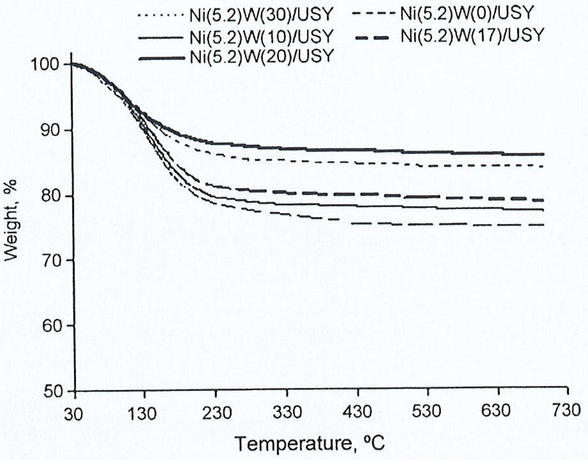

Fig. 4. TGA thermal stability results for NiW/USY catalyst with different tungsten loading.

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

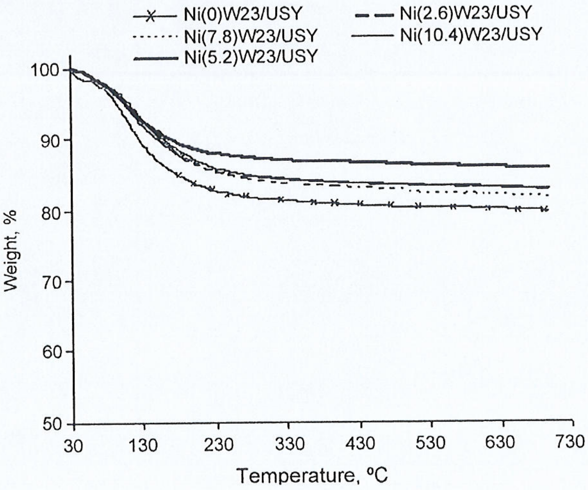

Fig. 5. TGA thermal stability results for NiW/USY catalyst with different nickel loading.

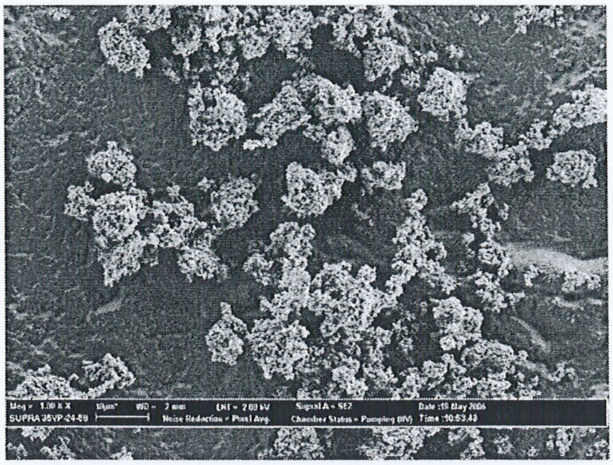

Fig. 6. Scanning electron micrographs of USY zeolite.

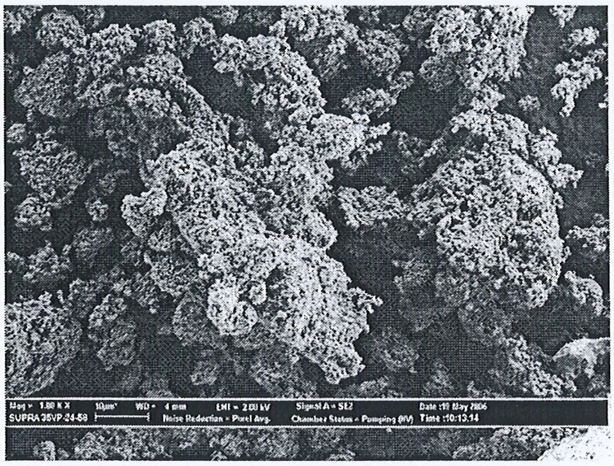

Fig. 7. Scanning electron micrographs of NiW/USY catalyst.

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.

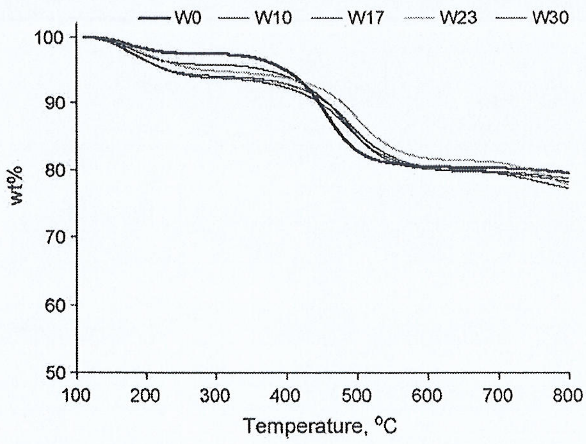

Fig. 8. Profiles of weight loss with temperature of NiW/USY coked catalyst with different tungsten loading.

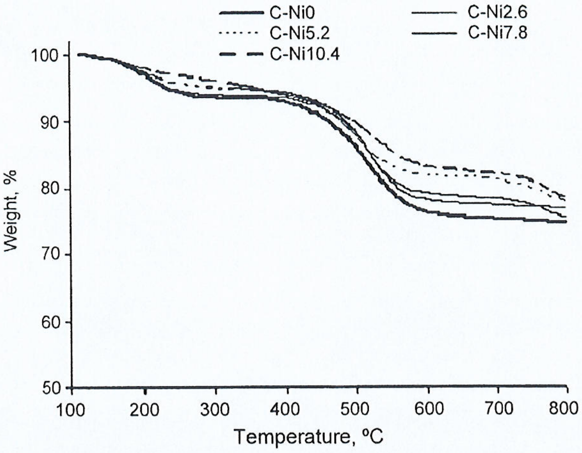

Fig. 9. Profiles of weight loss with temperature of NiW/USY coked catalyst with different nickel loading.

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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Characterization and hydrocracking of gas oil on sulfided NiW/MCM-48 catalysts

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Abstract

A series of mesoporous molecular sieve MCM-48 with SiO_2/Al_2O_3 ratios of 5, 25, 50, 75 and 125 was prepared and used as support for nickel and tungsten. The NiW/MCM-48 catalysts were prepared using the incipient wetness method. The 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 sample ratio of 0.04 (w/w). In all prepared samples, the catalyst activity and properties were improved with increasing alumina content and found that maximum values of a total conversion and liquid product (total distillate fuels) were obtained at silica/alumina molar ratio of 50. The catalysts were characterized by number of techniques and measurements, such as TPD–TGA acidity, TGA thermal stability, BET surface area, pore volume, pore size, XRD, SEM and TEM. Product distributions were also presented and discussed.

Keywords: Hydrocracking; Gas oil; NiW/MCM-48 catalyst; Shaking reactor

1. Introduction

Hydrocracking process is one of the most promising processes for production valuable petroleum products from heavy oil. The catalysts used for the hydrocracking process possess both hydrogenation and cracking functions. Active components and promoters sulphides provide hydrogenation function, while supports provide the cracking functions, where the cracking takes place on the acidic sites presented in the supports [1]. The development of highly active hydrocracking catalysts is one of the most important subjects in the petroleum industry and this can be achieved by a proper balance between these two functions [2].

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 and a surface area and pore size distribution appropriate for the desired reaction [3].

Various supports have been used in catalytic hydrocracking such as alumina, titania, silica, zirconia, activated carbon, clay, mixed oxides and zeolites [1,4–8]. The selection of a proper catalyst for a given high activity is a complex problem. While microporous zeolites such as Y, ZSM-5 and β are playing important roles in modern petrochemical industry for their abundant uniform microporous structures and strong intrinsic acidities, much attention is being given to the development of mesoporous zeolites that provide larger pores (>2 nm) to allow the conversion of large molecules and thus overcome the limitations of microporous zeolites.

To date, most of the published reports on mesoporous materials have included one-dimension mesoporous MCM-41 [9–15]. This is in part due to the difficulty of synthesizing of cubic phase MCM-48 materials [16]. Compared to the more familiar MCM-41, MCM-48 provides easier access to guest molecules due to its three-dimensional pore network. This decreases diffusion limitations and make MCM-48 more resistant to pore blocking [17]. MCM-48 contains uniform mesopores, which are larger than nanopores and smaller than macropores, which makes the material particularly suited to reactions involving large molecules, such as gas oil. Despite

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this advantage over MCM-41, the synthesis of high quality MCM-48 with controlled pore size is more challenging.

The synthesis of aluminium containing mesoporous MCM-48 with improved acidic characteristics is important in many catalytic applications. To improve the acidic characteristics of MCM-48, the alumina content (SiO_2/Al_2O_3 ratio) incorporated into framework is investigated. While increasing alumina content increases the activity of the catalyst, the lack of order resulting from silicate substitutions causes structure thermal instability. It is therefore important to optimise the SiO_2/Al_2O_3 ratio to achieve a reactive and stable catalyst.

The objectives of this work were to synthesize a series of mesoporous molecular sieve MCM-48 with different SiO_2/Al_2O_3 ratios and investigate its performance in hydrocracking of gas oil.

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

The synthesis of mesoporous molecular sieve MCM-48 with three-dimensional pore network was undertaken to the procedure reported by Sun and Coppens [17] and Oye et al. [18] with some modifications. 7.39 g of cetyltrimethylamonium bromide (CTMAB) was dissolved in 87.84 g distilled water and 1.21 g NaOH was added. 10.63 g of tetraethyl orthosilicate (TEOS) was subsequently added at room temperature. After 5 min of stirring, different amounts of aluminium nitrate (to give SiO_2/Al_2O_3 molar ratio of 5, 25, 50, 75 and 125) were added. The mixture was stirred vigorously for 1 h using a magnetic stirrer. The molar composition of gel was 1.0 CTAMB:2.5 TEOS:1.5 NaOH:244 H_2O. The gel formed was transferred into the Teflon bottle supplied by Nalge Nunc International Corporation, USA, and aged for 72 h at 110 °C. Then samples were filtered and washed with distilled water and dried at temperature of 110 °C. Finally, the samples were calcined at 550 °C for 5 h in a muffle furnace. The formed product was consequently impregnated with aqueous solution of NiW precursors $[(NH_4)_{10}(W_{12}O_{41})$ and $Ni(NO_3)_2{\cdot}6H_2O]$ 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 [6,7]. The composition of the catalyst is 23% wt of WO_3 and 5.2 wt.% of NiO. The MCM-48 samples were coded as M(X) where M referred to MCM-48 and X referred to SiO_2/Al_2O_3 molar ratio.

Prior to the reaction tests, the catalyst was pre-treated to increase its performance. About 1.2 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 settled 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 [19,20]. Then the sulfided catalyst was added directly to the shaking reactor and mixed with gas oil.

2.3. Characterization of catalysts

2.3.1. Nitrogen adsorption

Pore volume, surface area and average pore diameter of synthesized catalysts were measured using Autosorb1, Quantachrome Autosorb Automated Gas Sorption System supplied by Quantachrome. The samples were degassed for 3 h under vacuum at temperature of 300 °C using Autosorb1 instrument before measurements were performed [21]. The surface area was calculated using BET model, mesoporous and microporous areas were obtained from *t*-plot, pore volume and average pore size were obtained from BJH method. Adsorption isotherm was chosen as reference.

2.3.2. 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. 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 1 h (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 type of surface acidity corresponded to the temperature peaks. Weak acidity sites associated with the Lewis acid type occurred in the low temperature region of 100–200 °C whereas strong acid sites associated with the Bronsted acid type occurred in the high temperature region of 400–500 °C. From these data, it is possible to quantitatively identify the number of strong and weak acid sites in samples. The acidity was calculated by the following formula and reported in units of millimoles of acid sites per gram of catalyst

$$\text{acidity} = \frac{W\,(\text{g})(1/M_\text{b}\,(\text{mg/mmol}))(1000\,\text{mg}/1\,\text{g})}{W_\text{Z}\,(\text{g})} \qquad (1)$$

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 M_b is the molecular weight of base (isopropyl amine) (mg/mmol).

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.

2.3.3. X-ray diffraction

Powder X-ray diffraction (XRD) patterns of calcined mesoporous aluminosilicate (MCM-48) were obtained using Siemens D5000 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å) at 40 kV and 30 mA and scanning speed of 2°/min.

2.3.4. Transmission electron microscopy (TEM)

TEM images were carried out using Philips (CM12) transmission electron microscope equipped with Image Analyzer and operated at 80 kV. Samples were crushed and mixed with acetone in glass vials and shaken vigorously for few minutes and then kept for about 3 min to allow coarser particles to settle down and applied a drop of solution on a carbon film coated 400 mesh grid.

2.3.5. 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.

2.3.6. Elemental analysis

The elemental analysis of the synthesized MCM-48 materials was carried out using an inductive coupled plasma (ICP) spectrometer (Model PE, Optima 3000). A standard solution containing desired elements was used to normalize the analysis. The samples were dissolved in hydrofluoric acid solution in order to dissolve the crystalline oxides (SiO_2 and Al_2O_3).

2.4. The experimental setup

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 setup 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 (w/w). Hydrogen valve was opened to develop a total hydrogen atmosphere of 20 MPa 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:

$$\%\text{Conversion} = \frac{W_{GO} - W_R}{W_{GO}} \times 100 \tag{2}$$

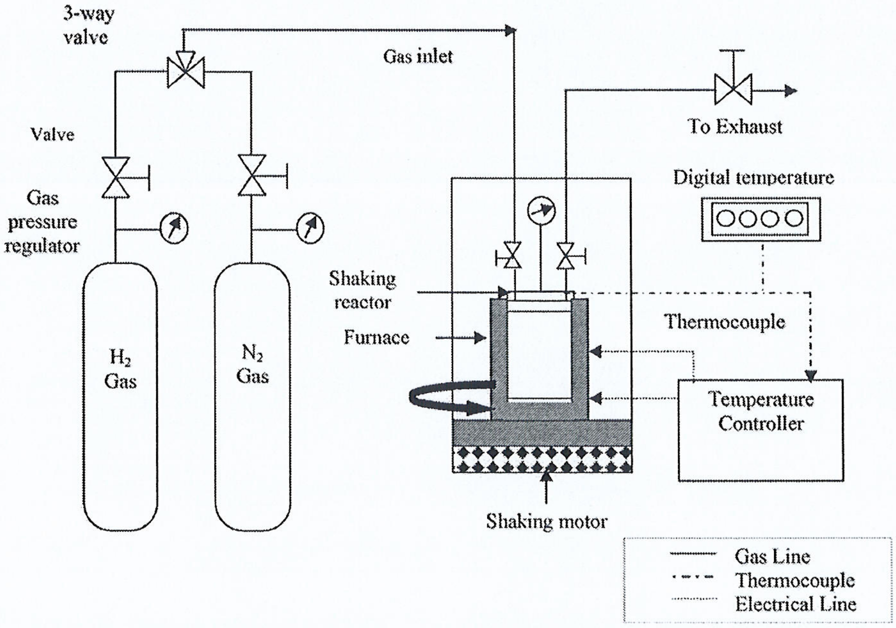

Fig. 1. Schematic diagram of the experimental setup for hydrocracking of petroleum gas oil.

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

$$Y_I = \frac{W_I}{W_{\mathrm{GO}}} \times 100 \qquad (3)$$

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

$$\text{catalyst to gas oil ratio} = \frac{W_{\mathrm{CA}}}{W_{\mathrm{GO}}} \qquad (4)$$

where W_{CA} is the weight of catalyst loaded.

2.5. 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 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 [12,22].

2.6. 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.

3. Results and discussion

3.1. Characterization of catalysts

Mesoporous aluminosilicate materials with three-dimensional pore network MCM-48 were synthesized by the conventional hydrothermal method. The ratio of alumina to silica was varied to study the effect of the alumina on the acidity properties of synthesized materials. The X-ray diffraction (XRD) pattern of calcined MCM-48 with different SiO_2/Al_2O_3 ratio is shown in Fig. 2. It was noted that all the prepared materials exhibited characteristics diffraction lines for MCM-48. It was noted that all the prepared materials exhibited characteristics diffraction lines for MCM-48. The high degree of ordering of mesoporous MCM-48 materials is confirmed by the presence of intense reflection in the mesoporous region for MCM-48. The mesophase contains two main reflections at 2θ of 2.1° and 2.7°, which confirm the mesostructural order in these samples. These results are in good agreement with reported ones [13,18]. The physical properties of synthesized MCM-48 materials are presented in Table 1. It can be seen from this table that the BET surface area and pore volume were increased as alumina content decreased while, average pore diameter was decreased. The obtained values were nevertheless similar to those reported in the literature and indicate high total porosity [17,18]. The percentage of microporous area was higher compared to the mesopoures area. This indicated that the different SiO_2/Al_2O_3 ratios in the precursor may affect the formation of the MCM-48 phase and not all alumina used in the synthesis mixture was incorporated into the framework (Table 1). The difficulty for the formation of the MCM-48 phase with high mesoporous is related to the high concentration of alumina in the prepared materials.

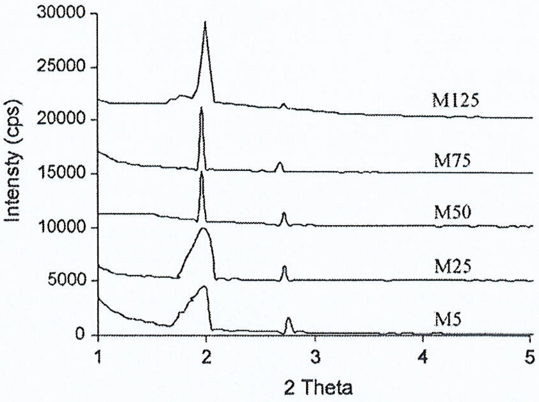

Fig. 2. XRD pattern for mesoporous molecular sieve MCM-48 with different SiO_2/Al_2O_3 ratio.

TGA is a useful tool to accurately detect desorption of basic molecules from zeolite as a function of temperature and the resulting data can be used to calculate the acid site strength and distribution [23,24]. Figs. 3 and 4 present the acidity results obtained from temperature programmed desorption (TPD) using TGA for MCM-48 and NiW/MCM-48 as a function of SiO_2/Al_2O_3 ratio, respectively. The total acidity and type of acid sites (weak and strong) were found to increase

Table 1
Physical properties of the MCM-48

Catalyst	Si/Al ratio	Surface area (m^2/g)	Mesoporous area (%)	Microporous area (%)	Pore volume (cm^3/g)	Average pore size (nm)
M5	12	185.0	44.7	55.3	0.194	4.20
M25	36	250.4	40.5	59.5	0.230	3.67
M50	67	462.0	34.7	65.3	0.410	3.55
M75	84	558.6	32.9	67.1	0.457	3.27
M125	132	814	30.0	70.0	0.657	3.23

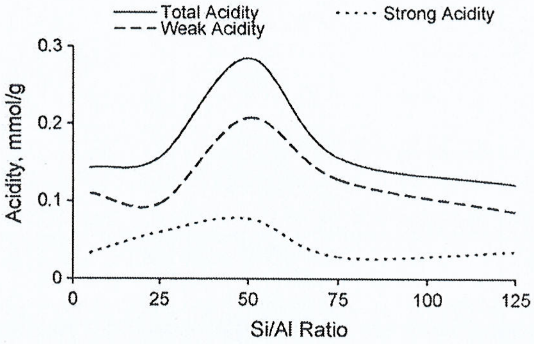

Fig. 3. TGA–TPD acidity for MCM-48 supports vs. SiO_2/Al_2O_3 ratio.

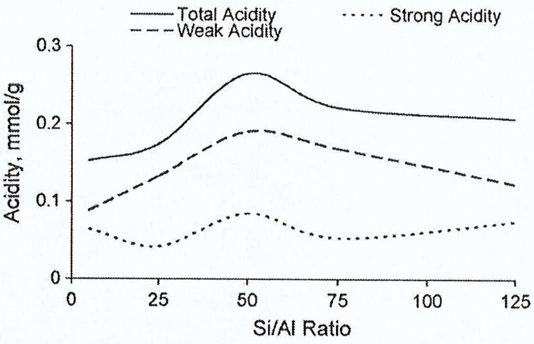

Fig. 4. TGA–TPD acidity for NiW/MCM-48 catalysts vs. SiO_2/Al_2O_3 ratio.

with Al content until SiO_2/Al_2O_3 ratio of 50 then decreased. The incorporation of Al into the framework generated acid sites which were able to interact with the base. The SiO_2/Al_2O_3 ratios of prepared samples presented in Table 1 indicated that alumina was present in the solid framework. The higher ratio of SiO_2/Al_2O_3 in the solid framework than that in the synthesis gel indicating that not all alumina used in the synthesis mixture was incorporated into the framework.

Figs. 5 and 6 show the experimental results of thermal stability analysis of calcined MCM-48 and NiW/MCM-48, respectively. According to the TGA curves, all synthesized materials showed very high thermal stability up to 730 °C and the weight loss below 100 °C is attributed to physically adsorbed water in the porous materials. Compared to all prepared MCM-48 (M5, M25, M50, M75, M125) and NiW/MCM-48 catalysts, M125 and NiW/M125 showed different behavior of decomposition in the first stage. The weight loss of M125 and NiW/M125 was higher in this stage. This is in good agreement with the porosity results which showed that M125 and NiW/M125 presented higher surface area compared to the other catalysts. Therefore, they adsorbed much amount of moisture.

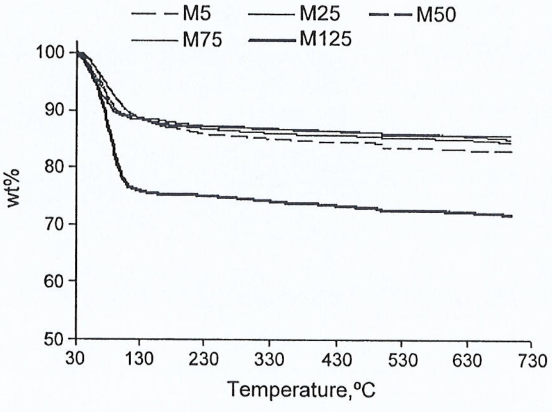

Fig. 5. TGA thermal stability results for MCM-48 with different SiO_2/Al_2O_3 ratio.

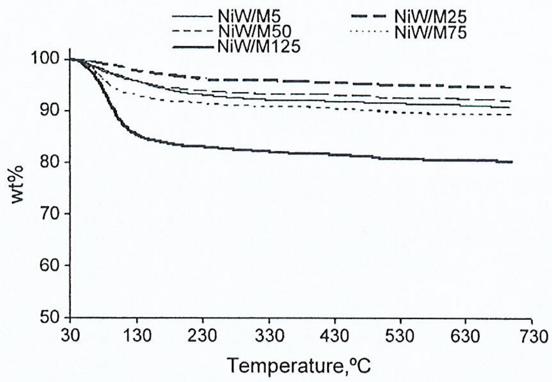

Fig. 6. TGA thermal stability results for NiW/MCM-48 with different SiO_2/Al_2O_3 ratio.

Scanning electron microscopy (SEM) of MCM-48 and NiW/MCM-48 with silica/alumina ratio of 50 is shown in Figs. 7 and 8, respectively. The SEM images showed that shape and size of crystalline particles were not uniform. For comparison, large sausage-like particles and big pore size were observed in the SEM image of MCM-48 (Fig. 7), while the NiW metals appeared to be primarily randomly distributed on the MCM-48 support and both fill up and plug some of pores (Fig. 8).

The TEM image of NiW/MCM-48 with different silica/alumina ratio is presented in Figs. 9–11. The structural characteristic of mesoporous molecular sieve MCM-48 can be observed clearly in the image. In addition, the order of mesopores with uniform size pore channels was noticed and found to increase with increase SiO_2/Al_2O_3 ratio. Furthermore, the TEM image showed the morphology of the NiW/MCM-48 catalyst and NiW particles attached on MCM-48 were clearly observed.

3.2. Performance of catalysts

Tables 2 and 3 present the analyses of the petroleum gas oil. The NiW/MCM-48 catalysts with different silica/alumina ratio were tested in hydrocracking of petroleum gas oil at reaction temperature of 450 °C, contact time of 90 min and catalyst to gas oil ratio of 0.04 (w/w). The hydrocracking results of MCM-48 and NiW/MCM-48 are presented in Tables 4 and 5. These results showed that the MCM-48 molecular sieves were active catalysts in gas oil hydrocracking. It is interesting to compare the activities of prepared catalysts with that of thermal cracking without catalyst. Thermal cracking showed lower conversion and distillate products. The conversion and total distillate fuels obtained from thermal cracking were 363.70 and 28.10 wt.%, respectively. Clearly, the cracking activity of NiW/MCM-48 catalysts is high in comparison to the unloaded MCM-48. This is

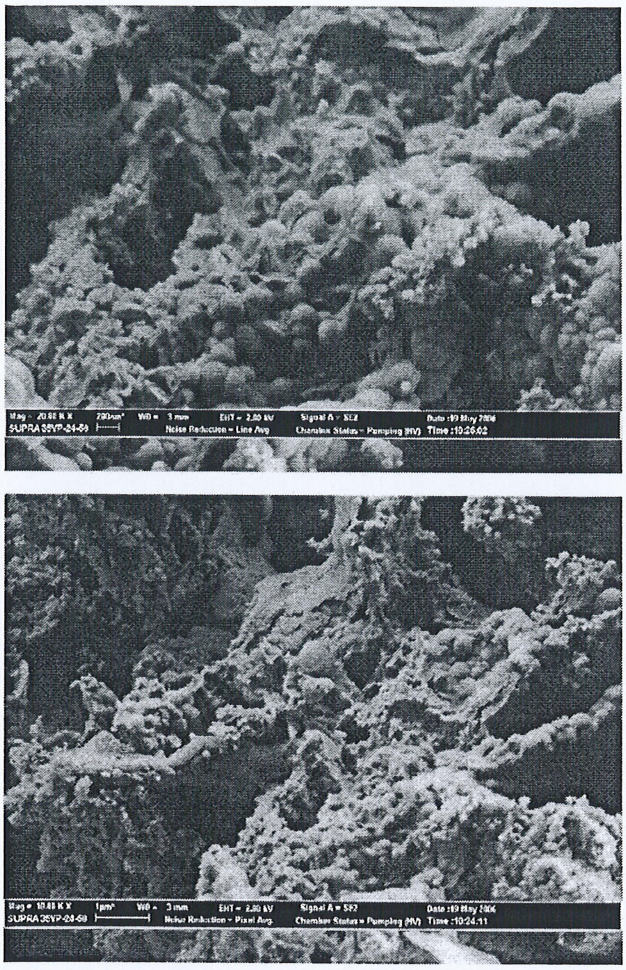

Fig. 7. Scanning electron micrographs of M50 support.

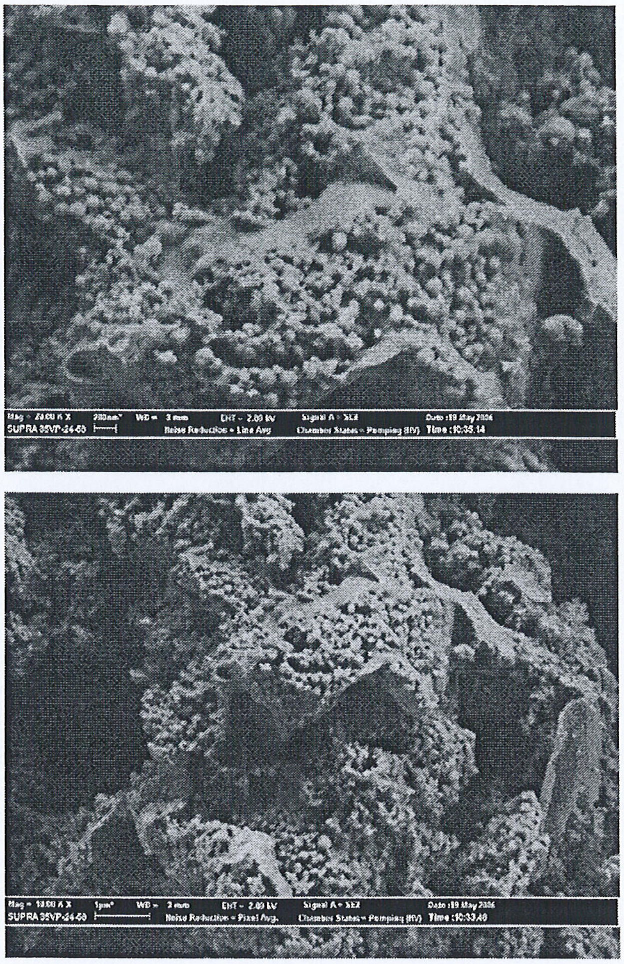

Fig. 8. Scanning electron micrographs of NiW/M50 catalyst.

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

Table 4
Gas oil hydrocraking over MCM-48 with different SiO_2/Al_2O_3 molar ratio

	Catalyst				
	M5	M25	M50	M75	M125
Conversion (wt.%)	42.56	43.61	50.23	45.11	43.35
Total distilled fuels (wt.%)	33.09	32.41	38.83	32.31	31.95
Gasoline (wt.%)	6.13	8.42	7.90	9.10	8.83
Kerosene (wt.%)	6.92	6.11	4.71	5.15	6.29
Diesel (wt.%)	20.04	17.88	26.22	18.06	16.83
Gas yield (wt.%)	5.77	6.73	7.4	8.27	7.7
Gas composition (mol%)					
CH_4	–	0.05	0.01	–	0.02
C_2H_4	0.57	0.27	0.32	0.25	0.25
C_2H_6	22.94	52.65	22.70	25.43	36.59
C_3H_6	5.43	1.58	3.40	2.32	2.18
C_3H_8	21.42	27.23	34.68	28.34	34.15
C_4H_{10}	23.91	13.38	26.62	26.64	23.42
$C_5^=$	25.73	4.84	12.27	17.02	3.39
Coke yield (wt.%)	3.7	4.47	4	4.53	3.7

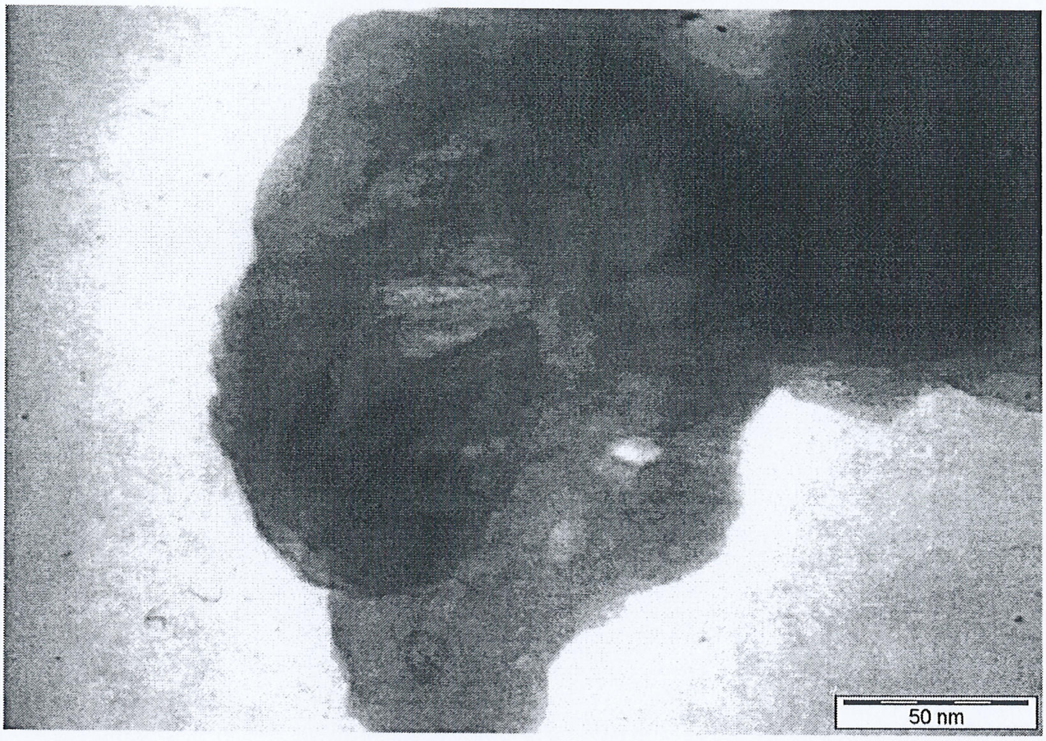

Fig. 9. TEM images of NiW/MCM-48 with SiO_2/Al_2O_3 ratio of 50.

due to the present the active component (*W*) and promoter (Ni). The active component (*W*) responsible for the principal chemical reaction, saturate aromatics in the feed, saturate olefins formed in the cracking, and protects the catalyst from poisoning by the coke. The role of the promoter (Ni) 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.

The total conversion and the product distribution were found to increase with decrease SiO_2/Al_2O_3 ratio till SiO_2/Al_2O_3 ratio of 50 then decreased. The acidity and porosity of catalysts influenced the product distribution obtained from the catalytic hydrocracking. NiW/MCM-48 with SiO_2/Al_2O_3 ratio of 50 (NiW/M50) possessed a high acidity, therefore, gave higher gas oil conversion and distilled products. It gave 64.31, 51.48, 15.58, 6.50 and of total conversion, total distilled products, gasoline, kerosene and diesel, respectively. The total conversion obtained in this study was 10–20 wt.% higher than that reported for the desulfurized vacuum gas oil over NiW/β-zeolite catalyst [1].

The yield of coke and gaseous products was in good agreement with the acidity changes happened during the change of SiO_2/Al_2O_3 ratio. This confirms the role of the strength of acid sites on the cracking reaction. Catalysts prepared with low

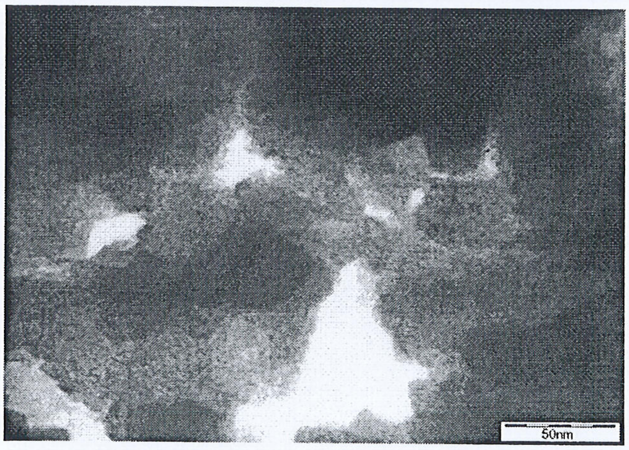

Fig. 10. TEM images of NiW/MCM-48 with SiO_2/Al_2O_3 ratio of 75.

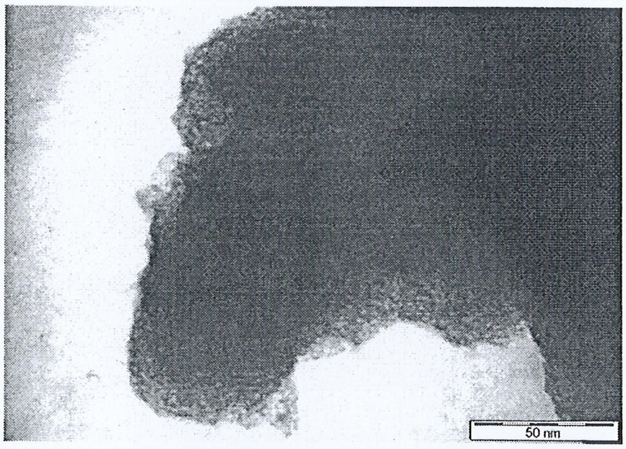

Fig. 11. TEM images of NiW/MCM-48 with SiO_2/Al_2O_3 ratio of 125.

Table 5
Gas oil hydrocraking over NiW/MCM-48 with different SiO_2/Al_2O_3 molar ratio

	Catalyst				
	NiW/M5	NiW/M25	NiW/M50	NiW/M75	NiW/M125
Conversion (wt.%)	52.61	62.49	64.31	60.23	59.44
Total distilled fuels (wt.%)	36.61	48.13	51.48	46.03	44.97
Gasoline (wt.%)	9.14	9.48	15.58	12.30	11.22
Kerosene (wt.%)	10.71	10.00	6.50	9.99	9.31
Diesel (wt.%)	16.76	28.65	29.40	23.74	24.44
Gas yield (wt.%)	11.00	10.13	8.83	10.37	10.80
Gas composition (mol%)					
CH_4	0.01	0.05	0.01	0	0.01
C_2H_4	0.20	0.27	0.16	0.29	0.20
C_2H_6	51.95	51.65	42.08	46.32	47.52
C_3H_6	1.42	1.58	1.32	1.63	2.88
C_3H_8	29.69	27.23	34.03	30.09	30.73
C_4H_{10}	16.73	15.38	22.4	18.93	18.66
$C_5^=$	0	3.84	0	2.74	0
Coke yield (wt.%)	5.00	4.23	4.00	3.83	3.67

SiO_2/Al_2O_3 ratios showed higher amounts of coke as compared to those having high silica to alumina ratios. Catalysts with low silica to alumina ratios are highly acidic and their acidity decreases with increase in silica to alumina ratio. High acidity tends to cause coking, which leads to deactivation.

3.3. Coked catalysts

TGA was used to obtain information about the nature of the coke deposited on different mesoporous molecular sieve MCM-48 catalysts. Figs. 12 and 13 presented profiles of weight loss with temperature of coked MCM-48 and NiW/MCM-48 catalysts, respectively. These curves showed that there are two general groups of coke formed in two temperature ranges, low range between 200 and 300 °C (soft coke) and high range between 400 and 500 °C (hard coke) for all catalysts used. The soft coke made up of oxygenated polyaromatic hydrocarbons below 250 °C and accumulated on mesopores and external surface of the zeolite [25]. While, the hard coke built up of less oxygenated polyaromatic compounds at temperature range of 400–550 °C and formed on Bronsted acid sites [26]. These results are indicated a more hard coke deposited over catalysts having high alumina content (low silica/alumina ratio), that is in good agreement with acid sites density.

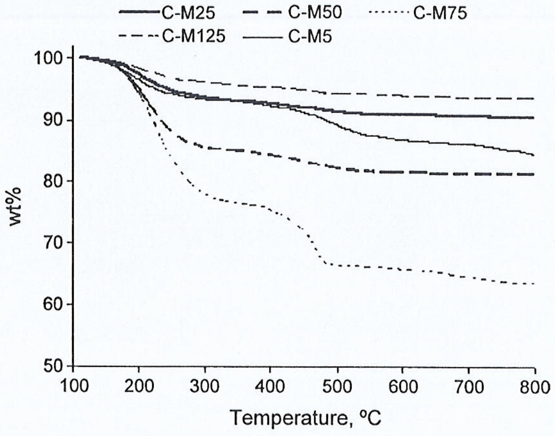

Fig. 12. Profiles of weight loss with temperature of coked MCM-48 with different SiO_2/Al_2O_3 ratio.

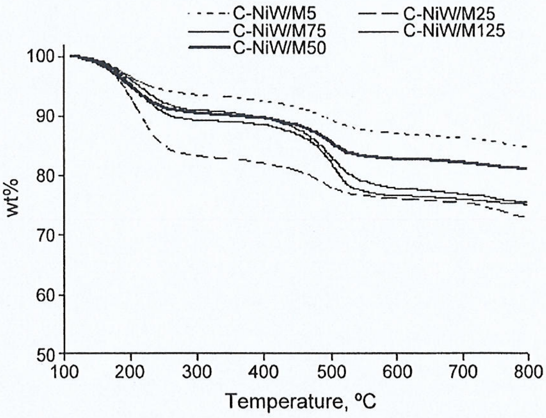

Fig. 13. Profiles of weight loss with temperature of coked NiW/MCM-48 with different SiO_2/Al_2O_3 ratio.

4. Conclusions

In summary, mesoporous molecular sieve MCM-48 with different SiO_2/Al_2O_3 ratios was synthesized via the conventional hydrothermal method. Different characterizations revealed the formation of MCM-48 material contains mesopore size in range of 3.23–4.20 nm. It has been shown that these materials provided a large surface area, improved mass transfer and relatively strong acidity, which resulted in high catalytic hydrocracking activity. Among prepared NiW/MCM-48 with different SiO_2/Al_2O_3 ratios (5, 25, 50, 75, 125) catalysts, NiW/MCM-48 with SiO_2/Al_2O_3 of 50 (NiW/M50) exhibited better catalytic activity for gas oil hydrocracking.

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HYDROCRACKING OF GAS OIL OVER $NiMo/Al_2O_3$ CATALYST

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ABSTRAK : *Nikel molybdum komersial yang disokong pada pemangkin alumina ($NiMo/Al_2O_3$) digunakan untuk pemetakan gas minyak pada keadaan operasi yang berbeza, suhu tindakbalas antara 300-400°C, masa sentuh 30-120 min dan pemangkin disuap pada nisbah 0-0.08 dengan menggunakan reaktor goncang tekanan tinggi yang baru direka. Kandungan produk utama ialah cecair, gas dan kok. Jumlah penukaran pada 59.61wt% dan nilai maksimun 51.91wt% produk cecair (jumlah bahan api sulingan) didapati pada suhu 450°C, 90 minit masa sentuh dan 0.04 nisbah pemangkin yang disuap. Taburan keluaran untuk eksperimen yang dijalankan pada keadaan berbeza ditunjukkan dan dibincang.*

ABSTRACT : Commercial nickel molybdenum supported on alumina catalyst ($NiMo/Al_2O_3$) was used for hydrocracking of gas oil under various operating conditions, reaction temperature in range 300-450°C, contact time 30-120 min and catalyst to feed ratio 0-0.08 using newly designed high-pressure shaking reactor. The product consists mainly from liquid, gas and coke. A total conversion of 59.61wt% and a maximum value of 51.91wt% of liquid product (total distillate fuels) were obtained at temperature of 450°C, 90 minutes contact time and 0.04 catalyst to feed ratio. Product distributions under different experimental conditions were presented and discussed.

KEYWORDS : Petroleum gas oil, $NiMo/Al_2O_3$ catalyst, a high-pressure shaking reactor.

Fig. 1 Not clear

INTRODUCTION

Since total crude oil demand is projected to grow and the oil reserves in the world are limited, there is a strong need to convert hydrocarbon feed stocks into lower boiling point products in greater yields and with more selectivity. In many parts of the world, light oil production is declining and heavy oil conversion, therefore, becomes increasingly important to maintain economic viability of these regions (Heinrich *et al.*, 1997). Recently, the price of crude oil has reached US $ 72 per barrel in the international market (www.answers.com/topic/oil-price-increases-of-2005) and the majority of machines and equipments being made at present are designed to run using liquid fuel. Therefore, it is important to extract much useful materials from crude oil.

Many investigators have reported the production of light fuels from cracking of heavy oils over different cracking catalysts (Sato *et al.*, 1999). The catalysts used for the hydrocracking process are formed by composting various transition metals with the solid support such as alumina, silica, alumina-silica, magnesia, carbon and zeolites Speight (1998). Tian *et al* (1998) used batch reactor for the hydrocracking of residue oil over dispersed water-soluble Ni-Mo catalyst and alumina supported Co-Mo catalyst. The experiments were done under low operating conditions, hydrogen pressure of 7 MPa, temperature of 340°C and time 30-240 min which is suitable for this reaction. Absi-Halabi *et al* (1998) studied the performance of a Ni-Mo-W $/\gamma$-Al_2O_3 catalyst using Kuwait vacuum residue as feed. The results revealed that the Ni-Mo-W catalyst was more active than either the Ni-Mo or Ni-W catalysts. The effect of catalyst composition on desulfurization reaction showed that both the NiMo and mixed NiMoW catalysts have nearly the same activity pattern toward desulfurization. Kaluza and Zdrail (2001) reported MoO_3 on activated carbon catalyst prepared by a new impregnation method for hydrodesulfurization process of thiophene. It was concluded that molybdenum trioxide was chemisorbed and highly dispersed 'monolayer' form up to loading of about 15% MoO_3 and then almost levelled off. Sato *et al.* (1999) carried out the hydrocracking of tetralin over NiW/USY zeolite catalysts for improvement of heavy oil upgrading catalysts using a 50-ml batch type reactor at temperature of 250-400°C, contact time of 3-180 min, catalyst load~~ed~~ of 0.3 g and operating pressure of 2-10.2 MPa. Their results revealed that the major reaction path in the initial period was found to differ from that later in the reaction. During the initial reaction period, tetralin is hydrocracked via a bimolecular process over both USY and NiW/USY. Subsequently, hydrocracking is catalyzed without the formation of heavy compounds. Hydrocracking over NiW/USY is superior to that over USY only in the longer reactions. This difference is due to the limited role of NiW sulphide in the hydrocracking of tetralin. NiW sulphide hydrogenates aromatic compounds so that the cycloparaffinic compounds produced are easily cracked over acid sites.

The aims of this work are to investigate the effect of operating condition (temperature, reaction time and catalyst to feed ratio) on hydrocracking of petroleum gas oil over commercial NiMo/ Al_2O_3 catalyst.

EXPERIMENTAL

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 analyses of the gas oil are given in Tables 1-2. 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.

Table 1. 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 2. 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

Catalyst

Commercial NiMo/Al_2O_3 catalyst was provided by Sud-Chemie AG Germany. The chemical composition and physical properties of the NiMo/Al_2O_3 catalyst are listed in Table 3-4. The catalyst was supplied in 1.3 mm size and crushed to the size range of 75-125 μm. 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~~ set 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 to again ~~to~~ purge the system (Ferrari *et al.*, 2001; Farag *et al.*, 1999).

Table 3. Chemical composition and physical properties of the NiMo / Al_2O_3 catalyst (Sud-Chemie AG Germany)

Property	Value
I. Chemical Composition (nominal)	
NiO, wt%	5.2 0.5
MoO_3, wt%	23.0 1.0
Na_2O, wt%	<0.05
Al_2O_3, wt%	balance
II. Physical Properties (typical)	
Particle Shape, TRIAX - Shaped Extrusions	
Particle Size, mm	1.3
Bulk Density, kg/m^3	790
Surface Area, m^2/g	175
Pore Volume, 1/kg	0.43
Side Crush Strength, N/kg	32
Loss of Attrition, wt.%	<5

→ *Supplied by manufacturer

Table 4. BET surface area, pore volume, average pore diameter and acidity of commercial NiMo / Al_2O_3 catalyst

BET surface area, m^2/g	175
Pore volume. cm^3/g	0.43
Average pore diameter, nm	9.8
Acidity, mmol / g_{Cat}	0.4228
Weak acidity, %	33.30
Strong acidity, %	66.70

The experimental set up

The 70-ml stainless steel high-pressure shaking reactor was manufactured with 15.24 cm long and 2.21cm 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.

About 30 g of desulphurized petroleum gas oil (DS-GO) sample was firstly poured into the reactor, and then the catalyst was added in different ratios from 0 to 0.08. Hydrogen valve was opened to develop a total hydrogen atmosphere after purging with nitrogen. The reactor was then heated to reaction temperature in the range 300-450°C. The reaction was carried out for a fixed period of time in the range 30-120 minutes 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 schematic diagram of the experimental set up using a high-pressure shaking reactor is shown in Figure 1.

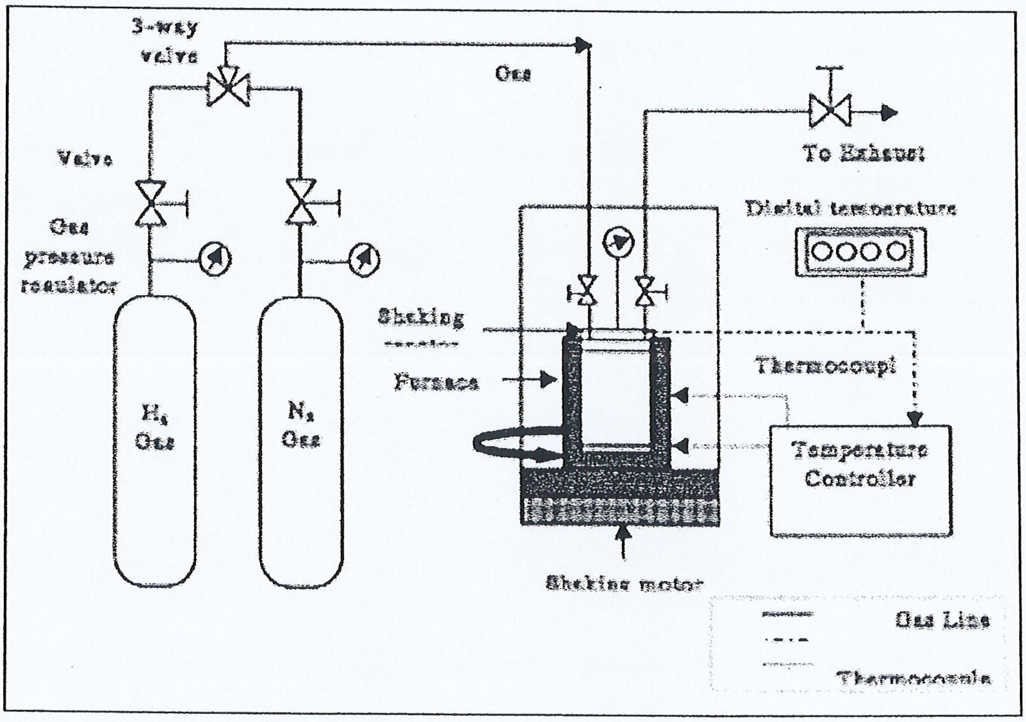

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***Figure 1.** Schematic diagram of the experimental set up for hydrocracking of petroleum gas oil using a high-pressure reactor*

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

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

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

$$\% \text{ } Y_I = \frac{W_I}{W_{GO}} \text{ X } 100 \qquad (2)$$

where Y_I is the yield of the product (wt%), I is 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.

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 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 recorded when the first drop of condensate was collected. The volume of condensate was taken down at the temperature 160, 200 and 240°C (Ooi *et al.*, 2004, Tian *et al.*, 1998).

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 x 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 present~~ed~~ 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.

Nitrogen Adsorption

Pore volume, surface area and average pore diameter of synthesized catalysts were measured using Autosorb1, Quantachrome Autosorb Automated Gas Sorption System supplied by Quantachrome. The samples were degassed for 3 h under vacuum at temperature of 300°C using Autosorb1 instrument before measurements were performed (Zhu *et al.*, 1999).

Scanning electron microscopy (SEM)

SEM studies were performed using Leica Cambridge Stereoscan 360, UK and Polaron for the coating system (sputter coating). SEM revealed quickly the normal size and shape of the particles, ~~and~~ providing a representative micrograph of the surface of supports and catalysts, and also to show the effect of metal on the particle size of supports. 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.

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 cm³/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. About 5 mg of the sample was placed in a platinum pan and heated under nitrogen gas stream of 20 cm³/min from ambient temperature to 500°C with a control heating rate of 20°C/min and hold at this temperature for 30 minutes. 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.

$$\text{Acidity} = \frac{W\left(\frac{1}{Mb}\right)\left(\frac{1000mg}{1g}\right)}{W_z} \qquad (4)$$

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

Elemental analyzer (EA)

The PE 2400 Series II CHNS Elemental Analyzer supplied by M/S Perkin Company, USA was used to determine H/C ratio and percentage of carbon, hydrogen, nitrogen and sulphur in the feed. About 1.5-2.5 mg of sample was put in a tin capsule unit. The maximum and minimum furnace temperatures were set at 975 and 500°C. The required gases are highly purified helium, oxygen and compressed air.

RESULTS AND DISCUSSION

Catalyst characterization

The commercial NiMo/Al_2O_3 catalyst was characterized using different techniques. The BET surface area, pore volume and average pore diameter are given in Table 2 and the pore size distribution of this catalyst is shown in Figure 2. As evident from ~~the~~ Figure 2, alumina-based catalyst has mesopores which are desirable for the hydrocracking of heavy compounds.

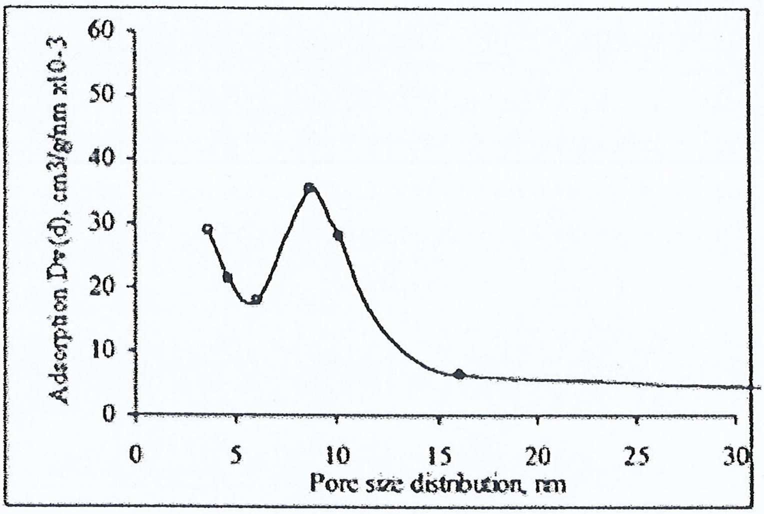

Figure 2. Pore size distribution of NiMo / Al_2O_3 catalyst

The acid sites of commercial NiMo/Al_2O_3 catalyst was carried out using TGA-TPD (temperature-programmed desorption). The number of weak and strong acid sites is ~~presents~~ shown in Table 2. The total number of acid sites, measured by the amount of isopropylamine, was 0.4228 mmol/g. The TGA-TPD profile is shown in Figure 3. The TGA-TPD measurements show that there are two acid sites, the peak in temperature range of 100-200°C is associated to the weak acid site (weak Lewis type) and the second peak found in temperature range of 300-400°C represents strong acid sites (strong Lewis type).

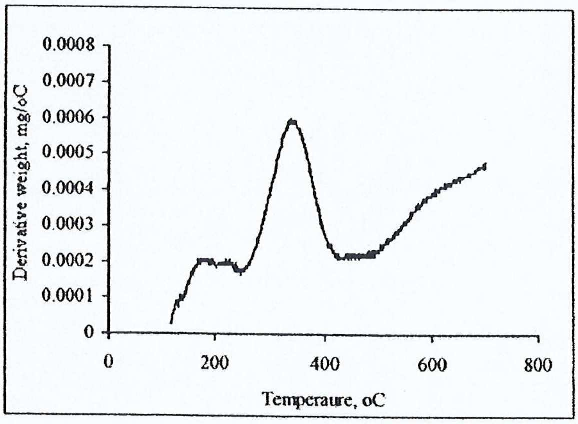

Figure 3. *TGA - TPD acidity for NiMo / Al_2O_3 catalyst*

Thermal gravity experiment was carried out to study the stability of the catalyst. Figure 4 shows the weight loss (TG) and DTG curves of commercial NiMo/Al_2O_3 catalyst. ~~It can be seen~~ two stages of thermal decomposition behaviour of the catalyst are seen: a plateau from 30 to 120°C with a little weight loss due to the moisture release and a main weight of catalyst in the last stage. That means the catalyst showed high thermal stability in the temperature range of 400-500°C. This stability of the catalyst is favourable to prevent thermal decomposition of the catalyst during the reactions and regeneration processes.

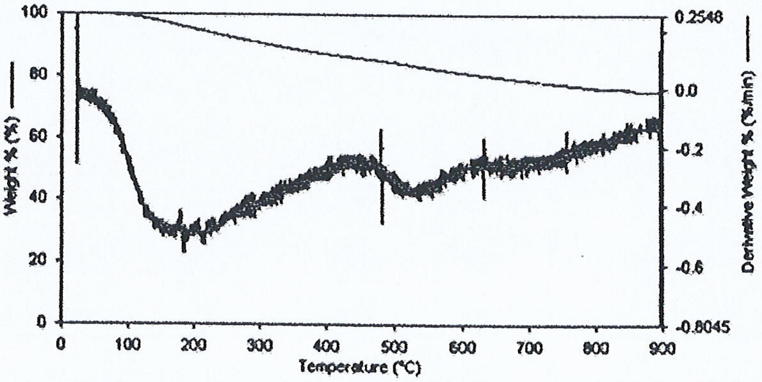

Figure 4. *TGA result for commercial NiMo / Al_2O_3 catalyst*

Figure 5 shows scanning electron microscopy of commercial NiMo/Al_2O_3 catalysts. It can be clearly ~~shown clearly~~ the metals appear to be primarily randomly distributed although some aggregation could be detected.

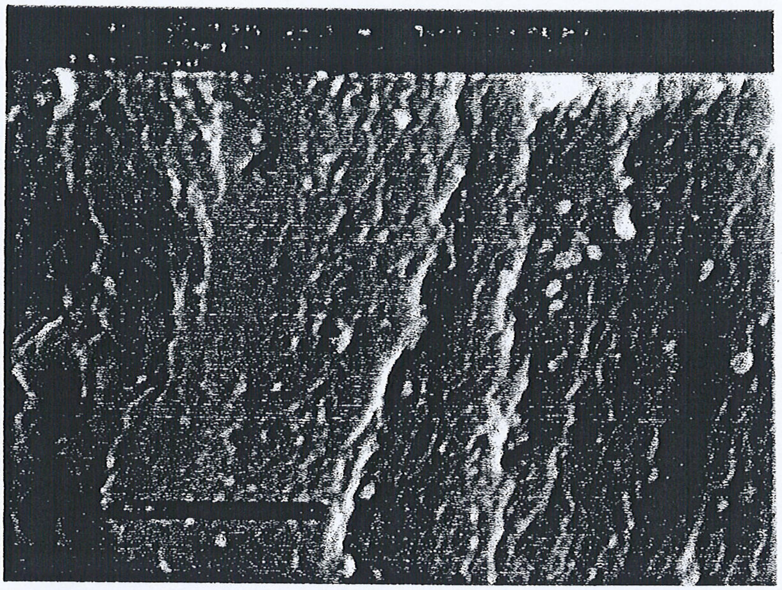

Figure 5. *SEM images for NiMo / Al_2O_3 catalyst, magnification is 5000 : 1*

Effect of reaction temperature

The analyses of the gas oil feed are given in Tables 1-2. Table 5 shows effect of reaction temperature on the total conversion and products distribution over NiMo/Al_2O_3 at 120 minutes time and 0.04 catalyst to feed ratio. A total conversion of 58.24 wt% was obtained at temperature of 450°C, while a minimum value of 14.50 wt% conversion was noticed at temperature of 300°C. A maximum value of 47.54 wt% of liquid product (total distillate fuels) was obtained at 450°C. The liquid product consists of gasoline, kerosene and diesel, where the yields of these products were 14.55, 14.42 and 18.57 wt%, respectively. Higher reaction temperature favours the hydrocracking reactions, which lead to formation of gas, coke and liquid consist~~s~~ing of higher percentage of the distillate fuels. At higher temperature, heavier compounds are cracked to product with lower boiling point. Usually at higher temperature more energy is provided to break the carbon-carbon bonds into shorter chains besides the action of the active catalyst that provide the active sites necessary for the cracking. Thus, the total conversion, distillate fuels ~~were~~ increased with increasing ~~of the~~ temperature. However, 10.70-wt% of both gas and coke were obtained under this temperature. Hence, the carbon-carbon bonds in liquid phase are cleaved to produce distillate fuels, gas and coke products, so these products and total conversion were found to increase with increasing reaction temperature.

Table 5. Gas oil conversion in the investigation of role of temperature range (Conditions : Reaction time = 120 min, Catalyst to oil ratio = 0.04)

Temperature, °C	300	350	400	450
Conversion (%)	14.50	20.00	28.80	58.24
Total distilled fuels	11.20	17.00	22.70	47.54
Gasoline	-	-	0.86	14.55
Kerosene	-	0.98	2.54	14.42
Diesel	11.20	16.02	19.30	18.57
Gas + Coke	3.30	3.00	6.10	10.70

Effect of contact time

Table 6 presents effect of contact time on total conversion and yield of products at 450°C temperature and 0.04 catalyst to feed ratio. It can be seen that total distillate products and diesel yield were increased with time until 90 minutes then decreased, while conversion and other wt% of distillate fuels were increased with reaction time. At lower reaction time, the complex compounds in gas oil were not completely cracked. The initial step in the hydrocracking of gas oil to lighter products involves free radical cracking (Gray, 1994). The free radicals and olefins resulting from this cracking are very reactive and can recombine to form heavy products. Stable oil and gas products resulting from primary cracking can also undergo free radical cracking and thus generate additional free radicals and olefins. These can further react to produce light and heavy products. The gas and coke products were constant with time until 90 minutes then increase. This increment of other wt% of distillate fuels at time above 90 minutes was happened because part of diesel product cracked to produce gasoline, kerosene, gas and coke products.

Table 6. Gas oil conversion in the investigation of role of contact time range (Conditions : Reaction temperature = 450°C, Catalyst to oil ratio = 0.04)

Time, min	30	60	90	120
Conversion (%)	33.26	52.25	59.61	58.24
Total distilled fuels	31.26	49.95	51.91	47.54
Gasoline	6.33	8.54	10.00	14.55
Kerosene	4.84	5.48	8.47	14.42
Diesel	20.09	35.93	33.44	18.57
Gas + Coke	2.00	2.30	7.70	10.70

Effect of catalyst to feed ratio

Table 7 shows total conversion and yield of products as a function of catalyst to feed ratio at 450°C reaction temperature and 90 minutes contact time. The total conversion was increased with catalyst to feed ratio and the optimum value of diesel and total distilled fuels was obtained at 0.04 ratio. The conversion and formation of distillate products are dominated by thermal cracking and the main role of catalyst is to enhance the uptake of hydrogen and prevent condensation and coking reactions (Gray, 1994). The hydrocracking reactions require significant breaking of carbon-carbon bonds. Breaking of C-C bonds relies on carbenium ion intermediates, promoted by the acid sites on the $NiMo/Al_2O_3$ catalyst surface.

Table 7. Gas oil conversion in the investigation of role of catalyst to feed ratio (Conditions : Reaction temperature = 450°C, Contact time = 90 minutes)

Catalyst to feed ratio	0	0.02	0.04	0.06	0.08
Conversion (%)	36.70	39.15	59.61	58.91	59.65
Total distilled fuels	28.10	32.25	51.91	52.61	51.85
Gasoline	6.13	8.78	10.00	10.70	11.85
Kerosene	7.60	6.73	8.47	9.34	8.48
Diesel	14.37	16.74	33.44	32.57	31.42
Gas + Coke	8.60	6.90	7.70	6.30	7.80

CONCLUSIONS

The hydrocracking of petroleum gas oil at reaction temperature in range 300-450°C, contact time 30-120 min and catalyst to feed ratio 0-0.08 was studied in high-pressure shaking reactor. Petroleum gas oil was converted to transportation fuels (gasoline, kerosene and diesel), gas and coke by hydrocracking over commercial $NiMo/Al_2O_3$ catalyst with total conversion of 59.61 wt% at temperature of 450°C, 90 minutes contact time and 0.04 catalyst to feed ratio. The effect of different operating conditions on hydrocracking reaction over commercial $NiMo/Al_2O_3$ catalyst was studied and found that 450°C reaction temperature, 90 min contact time and 0.04 catalyst to feed ratio are the most suitable operating conditions. Alumina-based catalyst showed very high thermal stability and has mesopores which are desirable for the hydrocracking of heavy compounds.

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Hydrocracking of gas oil over Ni-W, Ni-Mo, Co-W and Co-Mo catalysts supported on USY zeolite

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USY zeolite supported NiMo, CoMo, NiW and CoW catalysts was used to investigate the conversion of petroleum gas oil to distilled fuels. The catalysts were prepared using the incipient wetness method. The hydrocracking reaction was carried out in a high-pressure shaking reactor at reaction temperature of 450 oC, contact time of 90 minutes and catalyst to gas oil ratio of 0.04. It was found that over NiW/USY catalyst, the values of total conversion and yield of total distillate fuels were 63.35 and 52.35 wt%, respectively, compared to 47.81 and 36.58 wt% over unloaded USY zeolite. The hydrocracking activities of other USY-based catalysts were increased as follows, from most active to least active: NiW/USY> NiMo/USY> CoW/USY > CoMo/USY > USY. The catalysts were characterized by BET surface-area measurements, TGA-TPD acidity and TGA thermal stability.

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

Contents

1 Introduction

The global demand for crude oil has increased by 150% over the last 40 years and 20% in the past two decades to the current 80 million barrels per day and is projected to grow by 50% more in the next 20 years {Isaacs [1]}. The demand for lighter products (LPG, gasoline) and middle distillates (jet fuels, diesel) has grown steadily as a result of transportation demand, and the majority of machines and equipments being made at present are designed to run using liquid fuel. In petroleum refining, hydrocracking of heavy hydrocarbons has been carried out to produce high quality gasoline, jet fuel and diesel. Hydrocracking process needs dual function catalysts, hydrogenation and cracking functions. Active component and promoters sulphides provide hydrogenation function, while supports provide the cracking functions. Active components are commonly transition metal sulphides of an element in group VIB (i.e. molybdenum (Mo) or tungsten (W)) that responsible for the principal chemical reaction. The active components saturate aromatics in the feed, saturate olefins formed in the cracking, and protect the catalyst from poisoning by the coke. A promoter is a chemical compound such as nickel (Ni) and cobalt (Co) which when added results in desirable activity, selectivity or stability effects. 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 {Kabe *et al.* [2]}. 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 availability of sulphur anions, thus leading to more numerous of active sites in the reductive atmospheric of the hydrotreating processes. Mijoin {Mijoin [3]}

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and Breysse *et al.* {Breysse *et al.* [4]} 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 {Okamoto *et al.* [5]}.

Supports provide the cracking functions, 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 {Satterfield [6]}. 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 {Maesen *et al.* [7]}. Zeolites are defined as crystalline aluminosilicates, have been investigated and extensively used in industry. Zeolites have been successful because of their crystallinity, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity. The elementary building units of zeolites are SiO_4 and AlO_4 tetrahedra. Among the properties which are affected by the framework alumina content are the density of negative framework charges, cation-exchange capacity, the density of Bronsted acid sites, their strength and thermal stability {Weitkamp [8]}. For the majority of catalytic applications, medium or large pore zeolites will usually be preferred. In the processes which work under hydrogen pressure, such as hydrocracking of heavy petroleum distillates, the catalytic activity stems from the Bronsted acid sites rather than the Lewis acid sites. It is well known, due to the higher electronegativity of silicon compared to alumina, the strongest Bronsted acid sites in zeolites will occur on completely isolated AlO_4-tetrahedra. This is the reason why, upon dealumination of Y-zeolites with typical Si/Al ratio of 2.5, the catalytic activity generally increase up to Si/Al ratio of 10. In this region, the gain in acid strength overcompensate the decrease in the density of Bronsted acid sites {Weitkamp [8]}.

Many catalysts used for the hydrocracking process are formed by composting various transition metals with the catalyst supports such as alumina, silica, alumina-silica, magnesia, and zeolites {Navarro *et al.*, Ferdous *et al.* [9,16]}. High activity levels can be achieved with zeolites, which is not the case with conventional silica–alumina. The reason of the high activity and cracking selectivity of zeolites is their strong acidity which favours successive cracking reactions, and as a consequence, the formation of light products. It is an interesting line of research to use USY zeolite as catalyst support because there is lack in using it for hydrocracking of heavy oil.

The aim of this work was to investigate the performance of ultra-stable-Y (USY) zeolite for hydrocracking of petroleum gas oil at reaction temperature of 450^oC, 90 minutes contact time and 0.04 catalyst to gas oil ratio. The effect of different metals (NiMo, CoMo, NiW and CoW) loaded on USY zeolite on hydrocracking reaction was also studied. The catalysts characterizations using different techniques were presented and discussed.

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^oC was used in this investigation. This sample was obtained from Shell Refinery Company Bhd., Port Dickson, Malaysia. The properties of DS-GO reported previously {Alsobaai *et al.* [17]}. 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 NH4Cl solution and shacked for $24h$. 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^oC for $3h$ then calcined at 500^oC for $3h$. The chemical composition and physical properties of the USY zeolite provided by supplier reported previously {Alsobaai *et al.* [18]}. Synthesized NiMo, CoMo, NiW and CoW catalysts 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^oC overnight, followed by calcinations at 500^oC for $3h$ in a muffle furnace {Sato *et al.*; Hassan *et al.* [19,20]}. The composition of the catalyst was 23%

wt of MoO_3 (or WO_3) and 5.2% wt of NiO (or CoO). 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 settled to give a heating rate of $10^oC/min$. when the temperature of the reactor reached the desired temperature (360^oC), 5% H_2S balance hydrogen gas was allowed to pass through the system at 40 cm^3/min for $3h$. 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 {Farag *et al.*; Ferrari *et al.* [21,22]}.

2.3 The experimental set-up

The experimental set-up and procedure were explained and reported in our previous work {Alsobaai *et al.* [17]}. 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 ASTM distillation unit was supplied by Hotech Instruments Corp. The volume of condensate was taken down at the temperature 160, 200 and 240^oC {Tian *et al.*; Ooi *et al.* [23,24]}.

The gaseous products were analyzed using a gas chromatograph (Hewlett Packard, model No. 5890 series II) equipped with Porapak Q, 270 $cm - length \times 3.15mm$ stainless steel column (Supelco). The gases detected were hydrocarbons $C1 - C5$. The identity of resulting GC peaks was defined by injecting standard gases to FID detector.

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

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

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

$$Y_I = \frac{W_I}{W_{GO}} \times 100 \tag{2}$$

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

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

where W_{CA} is weight of catalyst loaded.

2.4 Characterization of catalysts

Pore volume, surface area and average pore diameter of synthesized catalysts were measured using Autosorb1, Quantachrome Autosorb Automated Gas Sorption System supplied by Quantachrome. The samples were degassed for $3h$ under vacuum at temperature of 300^oC using Autosorb1 instrument before measurements were performed {Zhu *et al.* [25]}.

Thermogravimetric analyzer (TGA) supplied by Perkin-Elemer, USA was used to study the thermal stability of the catalysts {Alsobaai *et al.* [26]}. 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^oC with a control heating rate of $20^oC/min$.

TGA-TPD (temperature–programmed desorption) was conducted on the same TGA instruments. 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:

$$Acidity = \frac{W\left(\frac{1}{Mb}\right)\left(\frac{1000mg}{1g}\right)}{Wz} \tag{4}$$

where W is the mass loss due to the desorption of base in the temperature of interest (g), W_Z is 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.

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 $(20 - 30nm$ thickness) in order to increase the conductivity and therefore the quality of the results.

TAB. 1: Characterization of USY-based catalysts

Catalyst	USY	NiMo/USY	CoMo/USY	NiW/USY	·CoW/USY
Surface area, m2/g	899	382	410	400	365
Mesoporous area, %	24.7	6.2	7.5	7.6	6.8
Microporous area, %	75.3	93.8	92.5	92.4	93.2
Pore volume, cm3/g	0.23	0.19	0.21	0.21	0.18
Average pore size (APS), nm	1.02	1.99	2.05	2.10	1.97

3 Results and Discussion

3.1 Nitrogen adsorption measurements

The BET surface areas, pore volumes and average pore diameters of support and catalysts are given in Tab. 1.

It can be seen that the surface areas of catalysts are lower than that of support. This is reasonable as the impregnated metals both fill up and plug some of pores, making less area available for nitrogen adsorption, and contribute to the weight of the catalyst, lowering the surface area measured on a weight basis. The pore volumes were estimated to be the liquid volume of nitrogen adsorbed at a relative pressure of 0.99. The pore volume of the support decreases after impregnated metals for the same reasons as the lower of the surface area.

3.2 TGA-TPD acidity measurements

The acid sites of commercial USY zeolite and prepared NiMo/USY, NiW/USY, CoMo/USY and CoW/USY catalysts were carried out using temperature programmed desorption (TPD). The TPD profiles of USY-based catalysts are shown in Fig. 1.

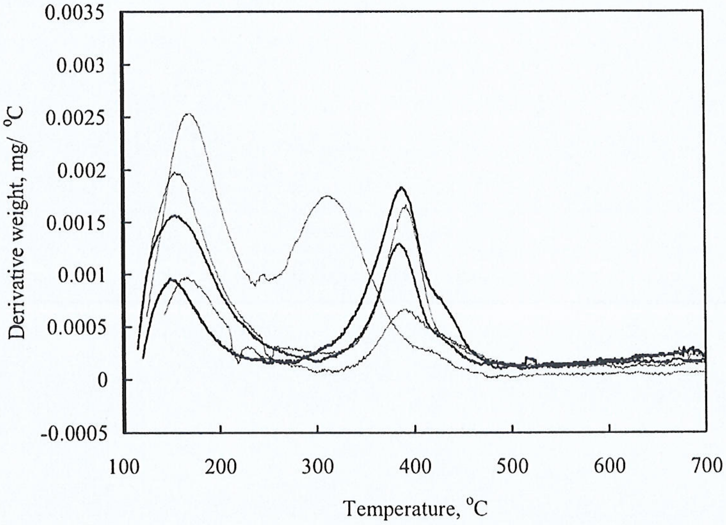

FIG. 1: TGA-TPD acidity for different catalysts used in this study.

The TPD measurements show that there are two acid sites in all USY-based catalysts, the peak in temperature range of $150 - 220^oC$ is associated to the weak acid site (Lewis type) and the second peak found in temperature range of $350 - 450^oC$ represents strong acid sites (Bronsted type). For commercial USY zeolite, two acid sites

TAB. 2: Total acidity, number of Bronsted and Lewis acid sites of USY and metal loaded USY.

Catalyst	USY	NiMo/USY	CoMo/USY	NiW/USY	CoW/USY
Acidity, mmol /gCat	1.79	1.01	0.973	1.30	1.16
Strong acidity, %	46.7	45.9	48.5	49.9	46.4
Weak acidity, %	53.3	54.1	51.5	50.1	53.6

are found in temperature range of 150 – 220 and 280 – 380^oC. The high-temperature peak of the USY samples in the TPD curves shifted to high temperatures when the metals are inserted, this maybe, because the metals interact with the zeolite Bronsted sites and induce stronger acidity or the metals themselves provide stronger acid sites , at the same time, masking the Bronsted acid sites of the support USY. The number of Bronsted and Lewis acid sites is presented in Tab. 2. The total number of acid sites, measured by the amount of isopropylamine, was much more significant on all USY-based catalysts. Comparing the total acidity of the catalysts used in this study, one can conclude that the relative acidity of these catalysts is in the order:

USY > NiW/USY > CoW/USY > NiMo/USY > CoMo/USY

3.3 Thermal stability analyzer (TGA)

Thermal gravity experiments were carried out to study the stability of the catalysts. Fig. 2 shows the weight loss (TG) curves of five tested samples: USY zeolite and prepared NiMo/USY, NiW/USY, CoMo/USY and CoW/USY catalysts.

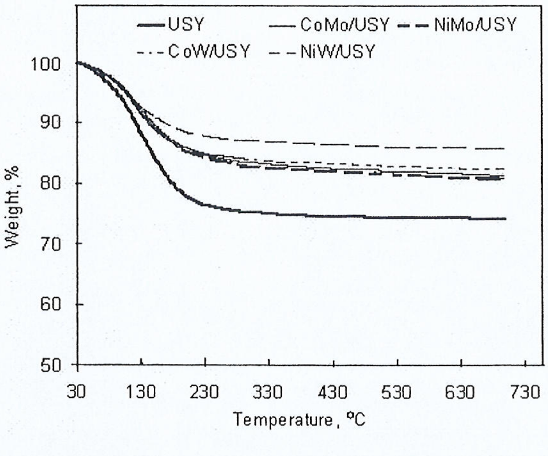

FIG. 2: TGA thermal stability results for USY-based catalysts.

It can be seen that two stages of thermal decomposition behaviour of the catalysts: a plateau from 30 to 120^oC with a little weight loss due to the moisture release and a main weight of catalysts in the last stage. That means all catalysts showed high thermal stability in the temperature up to 700^oC. This stability of the catalysts is favourable to prevent thermal decomposition of the catalysts during the reactions and regeneration process.

3.4 Scanning electron microscopy (SEM)

Scanning electron micrographs of USY zeolite and NiW/USY catalyst are presented in Fig. 3 and Fig. 4, respectively. SEM revealed quickly the normal size and shape of the particles, and providing a representative micrograph of the surface of USY zeolite and NiW/USY catalyst, and also showed the effect of metal on the particle size of supports. It is shown clearly the rougher surface of the USY zeolite and the NiW metals appear to be primarily randomly distributed although some aggregation could be detected.

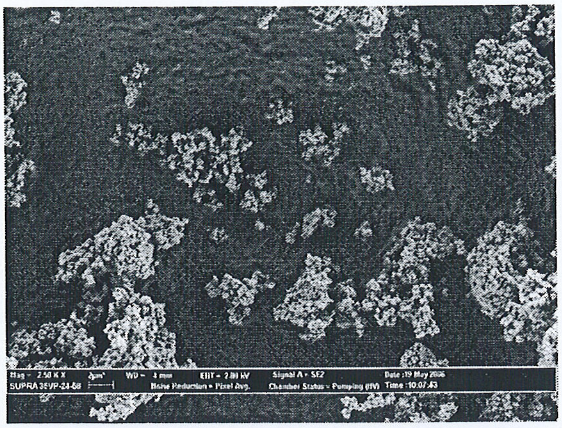

FIG. 3: Scanning electron micrographs of USY zeolite.

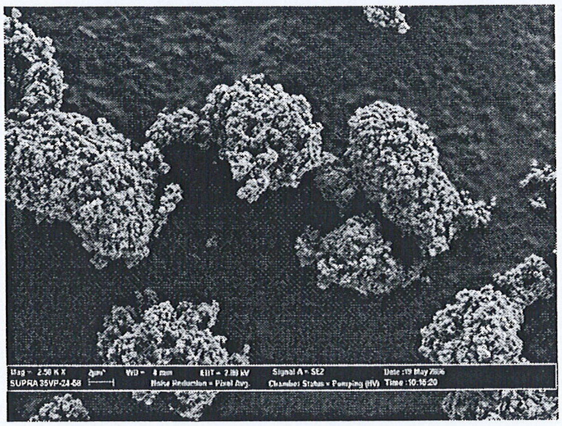

FIG. 4: Scanning electron micrographs of NiW/USY catalyst.

3.5 Coke analysis

Fig. 5 presents profiles of weight loss with temperature of coked USY, NiMo/USY, CoMo/USY, NiW/USY and CoW/USY catalysts.

It can be seen that there are two general groups of coke formed in two temperature ranges, low range between $150-250^oC$ (soft coke) and high range between $400-550^oC$ (hard coke) for all catalysts used. The soft coke made up of oxygenated polyaromatic hydrocarbons below 250^oC and accumulated on mesopores and external surface of the zeolite {Sahoo *et al.* [27]}. While, the hard coke built up of less oxygenated polyaromatic compounds at temperature range of $400-550^oC$ and formed on Bronsted acid sites {Antunes *et al.* [28]}.

Oxidation of coke initiated from 150^oC with steady decrease in weight until a sudden drop detected at $400-550^oC$. These temperatures reflected the ease or difficulty of the oxidation of coke and they were in the following order:

USY > NiW/USY > CoW/USY > NiMo/USY > CoMo/USY

3.6 Product distributions

Hydrocracking of petroleum gas oil was studied at reaction temperature of 450^oC, contact time of 90 minutes and catalyst to gas oil ratio of 0.04 using USY zeolite as support for NiMo, CoMo, NiW and CoW catalysts and their activity performance were investigated. The effect of catalysts types on the total conversion and products distribution obtained from hydrocracking of petroleum gas oil is shown in Tab. 3.

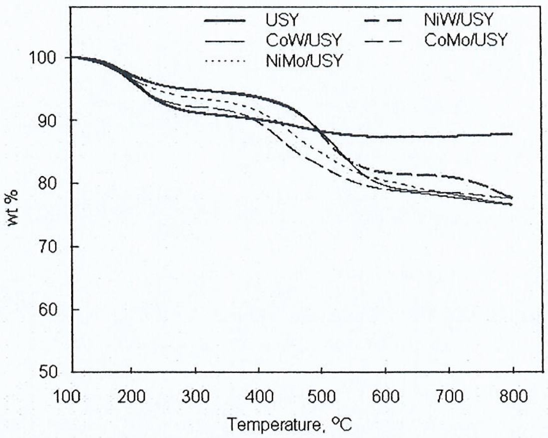

FIG. 5: Profiles of weight loss with temperature of coked catalysts.

TAB. 3: Product distribution of gas oil hydrocracking over USY-based catalysts.

Catalyst	USY	NiMo/USY	CoMo/USY	NiW/USY	CoW/USY
Conversion (wt.%)t	47.81	58.41	51.21	63.35	53.69
Total distilled fuels (wt.%)	36.58	49.98	39.68	52.35	41.99
Gasoline (wt.%)	8.13	14.29	13.49	11.52	12.92
Kerosene (wt.%)	7.16	8.67	4.09	5.14	10.44
Diesel (wt.%)	21.29	18.63	22.10	35.69	18.63
Gas yield (wt.%)	5.13	3.67	5.73	5.23	5.73
Gas composition (mol%)					
CH_4	0.01	0.02	0.01	0.01	-
C_2H_4	0.23	0.15	0.19	0.28	0.20
C_2H_6	38.98	39.45	37.35	42.42	41.19
C_3H_6	1.88	1.13	1.62	1.91	1.56
C_3H_8	31.50	32.68	31.27	29.15	30.32
C_4H_{10}	19.51	19.65	20.53	18.35	18.43
C5==	7.89	6.92	9.03	7.88	8.30
Coke yield (wt.%)	6.1	4.77	5.8	5.77	5.97

Within experimental error, all the catalysts exhibited a very stable activity for the conversion of gas oil, and yielded the same reaction products, namely gasoline, kerosene, diesel, gas and coke, although NiW/USY catalyst may be somewhat favoured. It is interesting to compare the activities of USY-based catalysts with that of commercial USY zeolite. Over NiW-loaded catalyst, the conversion and total distillate fuels were 15.54 and 15.77 *wt%*, respectively higher than USY zeolite. There are two roles of NiW sulphide, one is the supply of hydrogen to acid sites, a supply of hydrogen is essential for continuous hydrocracking, and the other role is hydrogenation of aliphatic and aromatic compounds to paraffinic and cycloparaffinic compounds, respectively. Among the catalysts, NiW/USY catalyst showed more hydrocracking activity compared to other catalysts in terms of conversion and total distillate products. The hydrocracking activities of other USY-based catalysts were slightly increased as follows, from most active to least active: NiW/USY> NiMo/USY> CoW/USY > CoMo/USY > USY. Higher hydrocracking activity of NiW/USY catalyst is due to its relatively high surface area with higher pore size and higher acidity which favours successive cracking reactions, and as a consequence, the formation of light products. Therefore, the catalytic activity of NiW/USY catalyst is correlated to its higher acidity with 50% strong acid sites (Bronsted acid sites). As known, to crack hydrocarbons, dual function catalysts, hydrogenation and cracking functions is needed. Supports provide the cracking functions, where the cracking takes place on acid sites.

The results show that the amount of both gas and coke obtained over all different types of the catalysts was around 8-12 wt% and the main gaseous products were hydrocarbons ethane, propane, C_4^+ and C_5^+.

4 Conclusions

In this present work, petroleum gas oil was converted to distilled fuels (gasoline, kerosene and diesel) by catalytic hydrocracking over NiMo, CoMo, NiW and CoW catalysts supported on commercial USY zeolite at reaction temperature of 450^oC, contact time of 90 minutes and catalyst to gas oil ratio of 0.04. A maximum value of liquid product (total distillate fuels) was obtained over NiW/USY catalyst, the values of total conversion and yield of total distillate fuels were 63.35 and 52.35 *wt%*, respectively, compared to 47.81 and 36.58 *wt%* over unloaded USY zeolite. The characterizations of catalysts were studied and product distributions over different catalysts were presented and discussed. NiW/USY catalyst possessed higher acidity with good balance between strong and weak acid sites. NiW/USY catalyst also showed very good thermal stability.

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Appendix C

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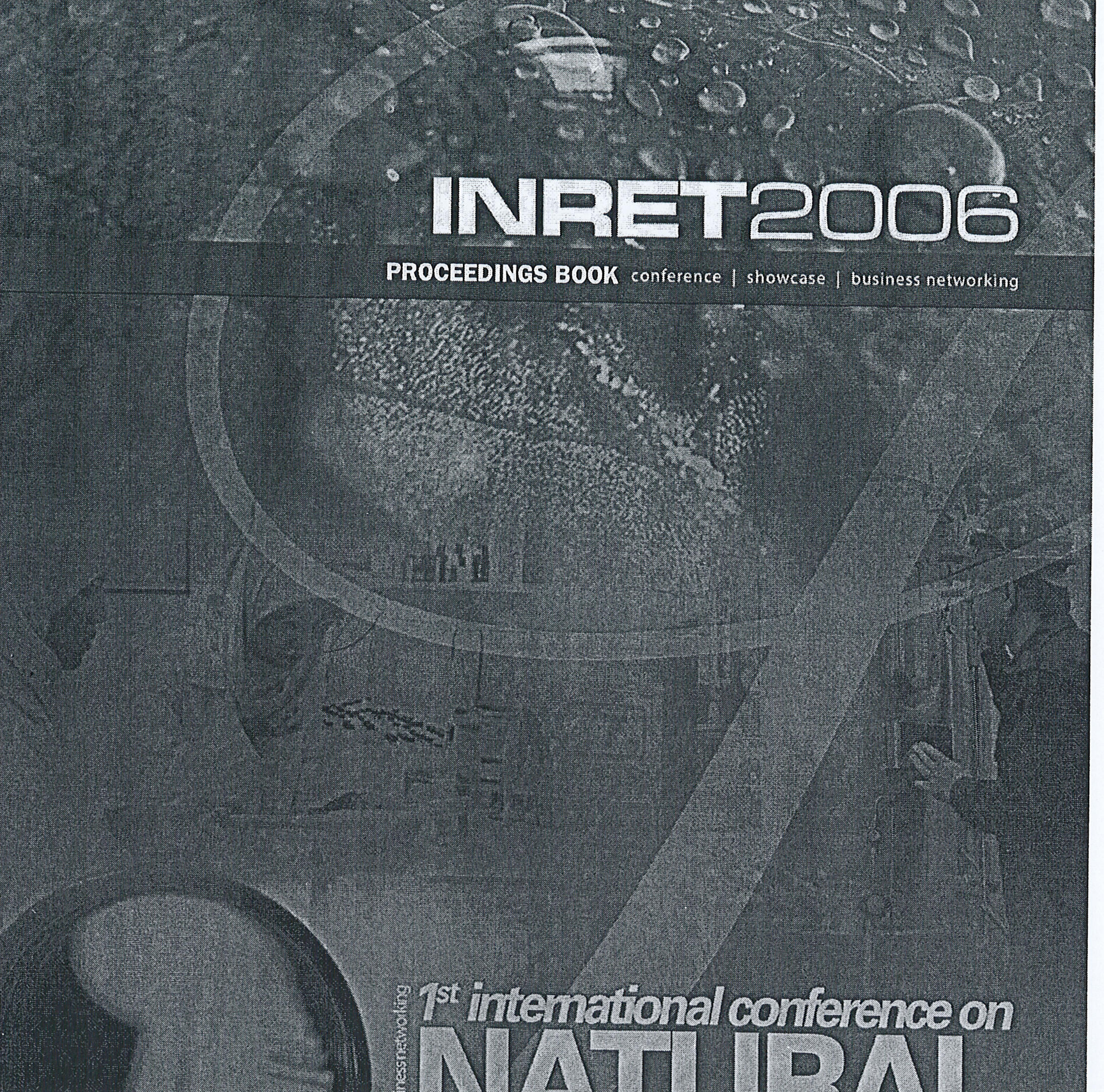
Appendix C

Publication in Proceeding/Conferences



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Value Added Products Through Process Intensification

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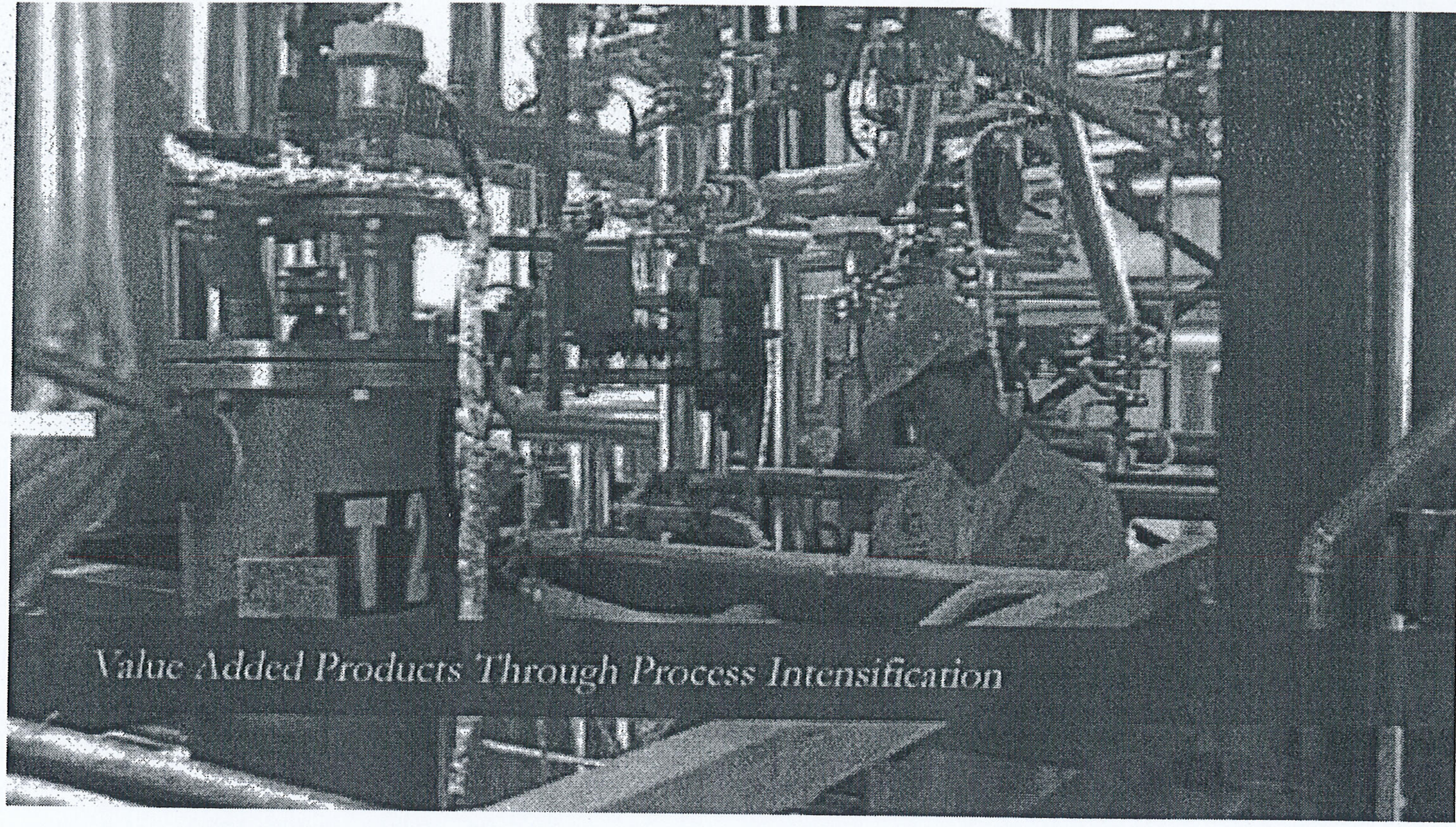

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The International Conference on Natural Resources Engineering and Technology 2006 (INRET 2006) with themed *Value Added Products Through Process Intensification* is initiated with the objective of providing a forum for academicians, researchers and professionals from government and corporate organizations to present their research findings and to exchange knowledge and information in pursuit of the latest developments relevant to chemical, biotechnology, pharmaceutical and agricultural industries. Knowledge and comprehension of such matters will lead to the advancement of innovative technologies in the respective fields.

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1st International Conference on Natural Resources Engineering and Technology (INRET 2006)

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24-25th July 2006; Putrajaya, Malaysia, 243-254

Hydrocracking of Gas Oil using USY-Zeolite-Based Catalyst

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Abstract

The conversion of petroleum gas oil to transportation fuels was investigated using NiMo, CoMo, NiW and CoW catalysts supported on commercial USY zeolite. The catalysts were prepared using the incipient wetness method. The reaction was carried out in a high-pressure shaking reactor at reaction temperature of 450 °C, contact time of 90 minutes and catalyst to sample ratio of 0.04. It was found that over NiW/USY catalyst, the values of total conversion and yield of total distillate fuels were 64.35 and 54.12 wt%, respectively, compared to 46.48 and 38.25 wt% over unloaded USY zeolite. The hydrocracking activities of other USY-based catalysts were increased as follows, from most active to least active: NiW/USY> NiMo/USY> CoW/USY > CoMo/USY > USY. The catalysts were characterized by TGA-TPD acidity, TGA thermal stability, and BET surface-area measurements.

Keywords: Petroleum gas oil, USY-based catalyst, high-pressure shaking reactor.

1.0 Introduction

The global demand for crude oil has increased by 150 % over the last 40 years and 20 % in the past two decades to the current 80 million barrels per day and is projected to grow by 50 % more in the next 20 years [1]. The demand for lighter products (LPG, gasoline) and middle distillates (jet fuels, diesel) has grown steadily as a result of transportation demand, and the majority of machines and equipments being made at present are designed to run using liquid fuel. In petroleum refining, hydrocracking of heavy hydrocarbons has been carried out to produce high quality gasoline, jet fuel and diesel. Hydrocracking process needs dual function catalysts, hydrogenation and cracking functions. Active component and promoters sulphides provide hydrogenation function, while supports provide the cracking functions. Active components are commonly transition metal sulphides of an element in group VIB (i.e. molybdenum (Mo) or tungsten (W)) that responsible for the principal chemical reaction. The active components saturate aromatics in the feed, saturate olefins formed in the cracking, and protect the catalyst from poisoning by the coke. A promoter is a chemical compound such as nickel (Ni) and cobalt (Co) which when added results in desirable activity, selectivity or stability effects. 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 [2]. 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 liability of sulphur anions, thus leading to more numerous of active sites in the reductive atmospheric of the hydrotreating processes.

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Mijoin [3] and Breysse et al. [4] 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 [5].

Supports provide the cracking functions, 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 [6]. 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 [7]. Zeolites are defined as crystalline aluminosilicates, have been investigated and extensively used in industry. Zeolites have been successful because of their crystallinity, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity. The elementary building units of zeolites are SiO_4 and AlO_4 tetrahedra. Among the properties which are affected by the framework alumina content are the density of negative framework charges, cation-exchange capacity, the density of Bronsted acid sites, their strength and thermal stability [8]. For the majority of catalytic applications, medium or large pore zeolites will usually be preferred. In the processes which work under hydrogen pressure, such as hydrocracking of heavy petroleum distillates, the catalytic activity stems from the Bronsted acid sites rather than the Lewis acid sites. It is well known, due to the higher electronegativity of silicon compared to alumina, the strongest Bronsted acid sites in zeolites will occur on completely isolated AlO_4-tetrahedra. This is the reason why, upon dealumination of Y-zeolites with typical Si/Al ratio of 2.5, the catalytic activity generally increase up to Si/Al ratio of 10. In this region, the gain in acid strength overcompensate the decrease in the density of Bronsted acid sites [8].

Many catalysts used for the hydrocracking process are formed by composting various transition metals with the catalyst supports such as alumina, silica, alumina-silica, magnesia, and zeolites [9-16]. High activity levels can be achieved with zeolites, which is not the case with conventional silica–alumina. The reason of the high activity and cracking selectivity of zeolites is their strong acidity which favours successive cracking reactions, and as a consequence, the formation of light products. It is an interesting line of research to use USY zeolite as catalyst support because it is play an important role in the catalysts used in hydrocracking process and there is lack in using it for hydrocracking of heavy oil. Sato et al. [17] carried out the hydrocracking of tetralin over NiW/USY zeolite catalysts using a 50 ml batch reactor. Their results revealed that hydrocracking over NiW/USY is superior to that over USY only in the longer reactions. This difference is due to the limited role of NiW sulphide in the hydrocracking of tetralin. NiW sulphide hydrogenates aromatic compounds so that the cycloparaffinic compounds produced are easily cracked over acid sites. The conversion over USY was almost the same as that over NiW/USY for the first 10 min and slightly lower in a longer reaction. Hassan et al. [18] compared between β and USY zeolite-based hydrocracking catalysts for hydrotreated vacuum gas oil (HT-VGO) using two series: γ-Al_2O_3 and β-zeolite (SiO_4/ Al_2O_3 molar ratio =24) in the first series and γ-Al_2O_3 and USY-zeolite (SiO_4/ Al_2O_3 =6) in the second series. Nickel and tungsten were loaded as active metals on these supports. They reported that β-zeolite-based catalysts showed higher cracking activity than USY-zeolite-based catalysts, while the total acidity (Lewis and Bronsted acid sites) of USY-zeolite-based catalysts higher than β-zeolite-based catalysts. This confirms that the catalytic cracking is not only dependent on the total acidity but also on the relative strength of acidic sites. Finally, they noted that the catalysts prepared by the physical mixing of zeolite with metal-loaded alumina show higher numbers of strong acid sites therefore consequently show higher cracking activity.

The aim of this work was to investigate the performance of ultra-stable-Y (USY) zeolite for hydrocracking of petroleum gas oil at reaction temperature of 450 °C, 90 minutes contact time and 0.04 catalyst to gas oil ratio. The effect of different metals (NiMo, CoMo, NiW and CoW) loaded on USY zeolite on hydrocracking reaction was also studied. The catalysts characterizations using different techniques were presented and discussed.

2.0 Materials & Method

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 and °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 NiMo, CoMo, NiW and CoW catalysts 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 [17,18]. The composition of the catalyst was 23% wt of MoO_3 (or WO_3) and 5.2% wt of NiO (or CoO). 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 settled 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 [19,20].

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

Zeolite type	USY
Commodity	HSZ-320NAA
SiO_2/Al_2O_3 mole ratio	5.5
Na_2O/Al_2O_3 mole ratio	1.00
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 2.21cm 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 minutes after the reactor working temperature and pressure were attained.

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

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

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

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

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

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

where W_{CA} is weight of catalyst loaded.

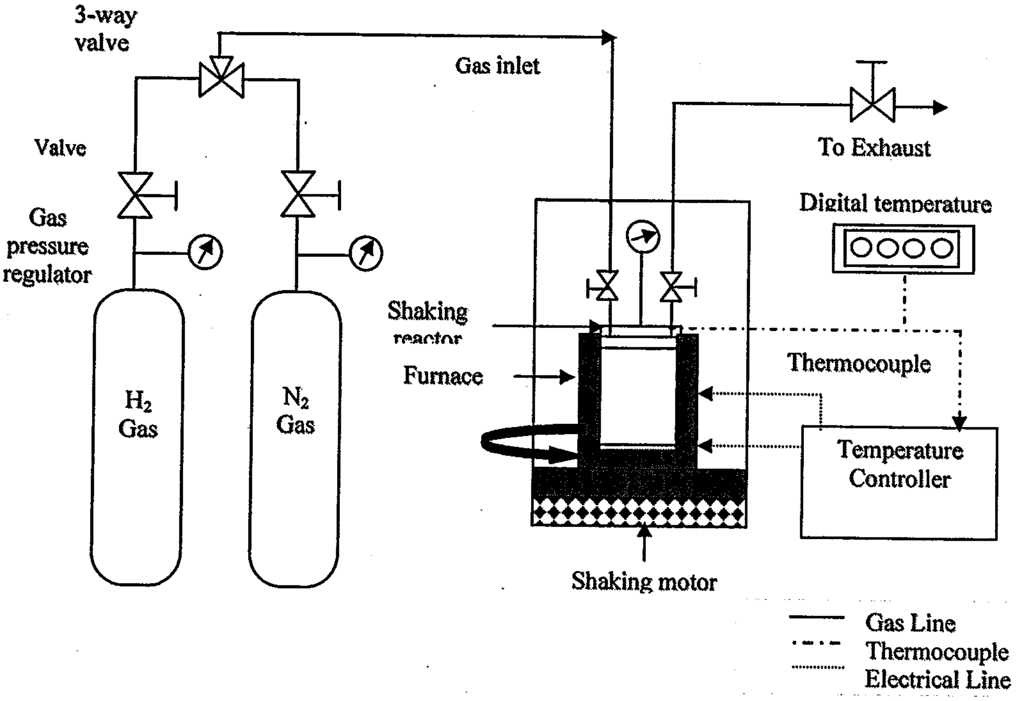

Figure 1 Schematic diagram of the experimental set up for hydrocracking of petroleum gas oil

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 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 product 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 [21,22].

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, 270cm-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. Characterization of catalysts

2.6. 1 Nitrogen Adsorption

Pore volume, surface area and average pore diameter of synthesized catalysts were measured using Autosorb1, Quantachrome Autosorb Automated Gas Sorption System supplied by Quantachrome. The samples were degassed for 3 h under vacuum at temperature of 300 °C using Autosorb1 instrument before measurements were performed [23].

2.6.2. 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. 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 minutes. 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:

$$Acidity = \frac{W\left(\frac{1}{Mb}\right)\left(\frac{1000mg}{1g}\right)}{Wz} \qquad (4)$$

where W is the mass loss due to the desorption of base in the temperature of interest (g), W_Z is 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.

3.0 Results and Discussion

3.1. Nitrogen adsorption measurements

The BET surface areas, pore volumes and average pore diameters of support and catalysts are given in Table 2. It can be seen that the surface areas of catalysts are lower than that of support. This is reasonable as the impregnated metals both fill up and plug some of pores, making less area available for nitrogen adsorption, and contribute to the weight of the catalyst, lowering the surface area measured on a weight basis. The pore volumes were estimated to be the liquid volume of nitrogen adsorbed at a relative pressure of 0.99. The pore volume of the support decreases after impregnated metals for the same reasons as the lower of the surface area.

Table 2 Characterization of USY and metal loaded USY.

Catalyst	USY	NiMo/USY	CoMo/USY	NiW/USY	CoW/USY
Surface area, m^2/g	899	382	410	400	365
Mesoporous area, %	24.7	6.2	7.5	7.6	6.8
Microporous area, %	75.3	93.8	92.5	92.4	93.2
Pore volume, cm^3/g	0.23	0.19	0.21	0.21	0.18
Average pore size (APS), nm	1.02	1.99	2.05	2.10	1.97
Acidity, mmol /g_{Cat}	1.79	1.01	0.973	1.30	1.16
Strong acidity, %	46.7	45.9	72.5	49.9	46.4
Weak acidity, %	53.3	54.1	27.5	50.1	53.6

3.2. TGA-TPD acidity measurements

The acid sites of commercial USY zeolite and prepared NiMo/USY, NiW/USY, CoMo/USY and CoW/USY catalysts were carried out using temperature programmed desorption (TPD). The TPD profiles of USY-based catalysts are shown in Fig. 2. The TPD measurements show that there are two acid sites in all USY-based catalysts, the peak in temperature range of 150-220°C is associated to the weak acid site (Lewis type) and the second peak found in temperature range of 350-450°C represents strong acid sites (Bronsted type). For commercial USY zeolite, two acid sites are found in temperature range of 150-220 and 280-380°C. The number of Brønsted and Lewis acid sites is presents in Table 2. The total number of acid sites, measured by the amount of isopropylamine, was much more significant on all USY-based catalysts. Comparing the total acidity of the catalysts used in this study, one can conclude that the relative acidity of these catalysts is in the order:
USY > NiW/USY> CoW/USY > NiMo/USY > CoMo/USY

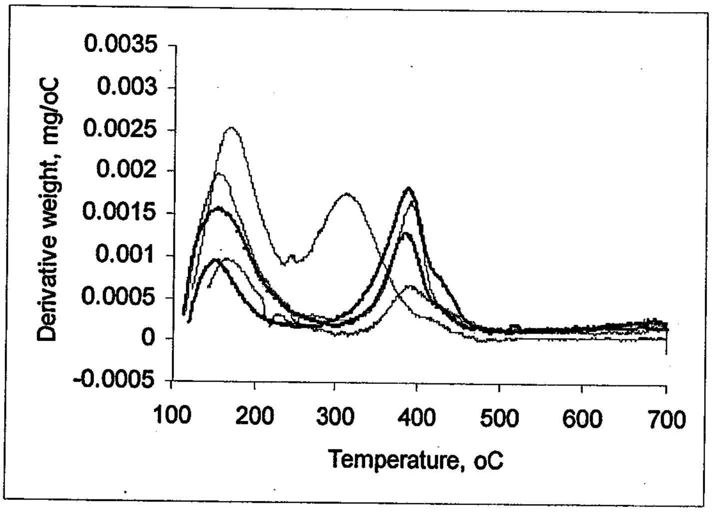

Figure 2 TGA-TPD acidity for different catalysts used in this study

3.3. Thermal stability analyzer (TGA)

Thermal gravity experiments were carried out to study the stability of the catalysts. Fig. 3 shows the weight loss (TG) curves of five tested samples: USY zeolite and prepared NiMo/USY, NiW/USY, CoMo/USY and CoW/USY catalysts. It can be seen that two stages of thermal decomposition behaviour of the catalysts: a plateau from 30 to 120 °C with a little weight loss due to the moisture release and a main weight of catalysts in the last stage. That means 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.

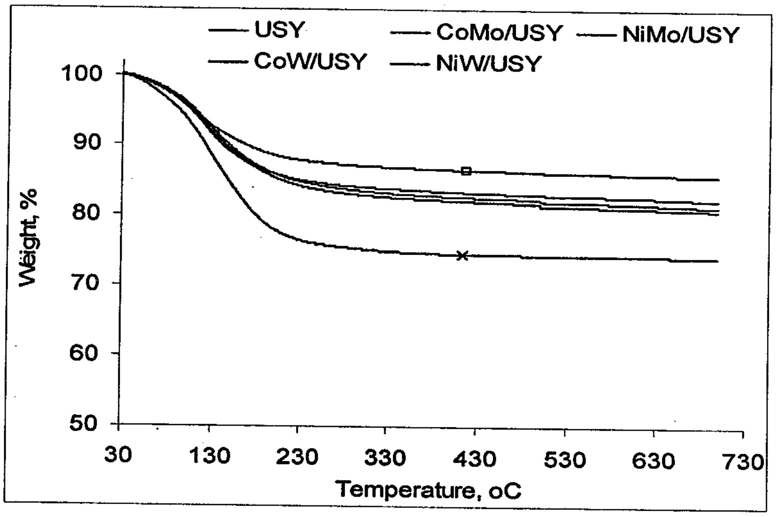

Figure 3 TGA thermal stability results for USY-based catalysts

3.4. Coke analysis

Fig. 4 presents profiles of weight loss with temperature of coked USY, NiMo/USY, CoMo/USY, NiW/USY and CoW/USY catalysts. It can be seen that there are two general groups of coke formed in two temperature ranges, low range between 150-250 °C (soft coke) and high range between 400-550 °C (hard coke) for all catalysts used. The soft coke made up of oxygenated polyaromatic hydrocarbons below 250 °C and accumulated on mesopores and external surface of the zeolite [24]. While, the hard coke built up of less oxygenated polyaromatic compounds at temperature range of 400-550 °C and formed on Bronsted acid sites [25].

Oxidation of coke initiated from 150 °C with steady decrease in weight until a sudden drop detected at 400-550 °C. These temperatures reflected the ease or difficulty of the oxidation of coke and they were in the following order:
USY > NiW/USY > CoW/USY > NiMo/USY > CoMo/USY.

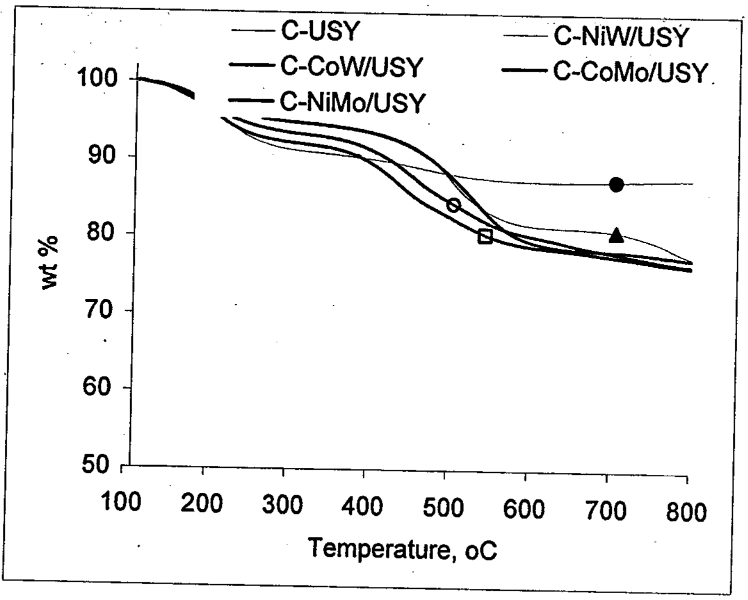

Figure 4 Profiles of weight loss with temperature of coked catalysts.

3.5. Product distributions

The analyses of the gas oil are given in Tables 3 and 4. Hydrocracking of petroleum gas oil was studied at reaction temperature of 450 °C, contact time of 90 minutes and catalyst to gas oil ratio of 0.04 using USY zeolite as support for NiMo, CoMo, NiW and CoW catalysts and their activity performance were investigated. The effect of catalysts types on the total conversion and products distribution obtained from hydrocracking of petroleum gas oil is shown in Table 5. Within experimental error, all the catalysts exhibited a very stable activity for the conversion of gas oil, and yielded the same reaction products, namely gasoline, kerosene, diesel, gas and coke, although NiW/USY catalyst may be somewhat favoured. It is interesting to compare the activities of USY-based catalysts with that of commercial USY zeolite. Over NiW-loaded catalyst, the conversion and total distillate fuels were 15.54 and 15.77 wt%, respectively higher than USY zeolite. There are two roles of NiW sulphide, one is the supply of hydrogen to acid sites, a supply of hydrogen is essential for continuous hydrocracking, and the other role is hydrogenation of aliphatic and aromatic compounds to paraffinic and cycloparaffinic compounds, respectively. Among the catalysts, NiW/USY catalyst showed more hydrocracking activity compared to other catalysts in terms of conversion and total distillate products. The hydrocracking activities of other USY-based catalysts were slightly increased as follows, from most active to least active: NiW/USY> NiMo/USY> CoW/USY > CoMo/USY > USY. Higher hydrocracking activity of NiW/USY catalyst is due to its relatively high surface area with higher pore size and higher acidity which favours successive cracking reactions, and as a consequence, the formation of light products. Therefore, the catalytic activity of NiW/USY catalyst is correlated to its higher acidity with 50 % strong acid sites (Bronsted acid sites). As known, to crack hydrocarbons, dual function catalysts, hydrogenation and cracking functions is needed. Supports provide the cracking functions, where the cracking takes place on acid sites.

The results show that the amount of both gas and coke obtained over all different types of the catalysts was around 8-12 wt% and the main gaseous products were hydrocarbons ethane, propane, C_4^+ and C_5^+.

Table 3 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 4 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

Table 5 Product distribution of gas oil hydrocracking over USY-based catalysts.

Catalyst	USY	NiMo/USY	CoMo/USY	NiW/USY	CoW/USY
Conversion (wt.%)	47.81	58.41	52.21	63.35	53.69
Total distilled fuels (wt.%)	36.58	49.98	39.68	52.35	41.99
Gasoline (wt.%)	8.13	14.29	15.49	11.52	12.92
Kerosene (wt.%)	7.16	8.67	4.09	5.14	10.44
Diesel (wt.%)	21.29	18.63	20.10	35.69	18.63
Gas yield (wt.%)	5.13	3.67	6.73	5.23	5.73
Gas composition (mol%)					
CH_4	0.01	0.02	0.01	0.01	-
C_2H_4	0.23	0.15	0.19	0.28	0.20
C_2H_6	38.98	39.45	37.35	42.42	41.19
C_3H_6	1.88	1.13	1.62	1.91	1.56
C_3H_8	31.50	32.68	31.27	29.15	30.32
C_4H_{10}	19.51	19.65	20.53	18.35	18.43
$C_5^{=}$	7.89	6.92	9.03	7.88	8.30
Coke yield (wt.%)	6.1	4.77	5.8	5.77	5.97

4.0 Conclusion

In this present work, petroleum gas oil was converted to distilled fuels (gasoline, kerosene and diesel) by catalytic hydrocracking over NiMo, CoMo, NiW and CoW catalysts supported on commercial USY zeolite at reaction temperature of 450 °C, contact time of 90 minutes and catalyst to gas oil ratio of 0.04. A maximum value of liquid product (total distillate fuels) was obtained over NiW/USY catalyst, the values of total conversion and yield of total distillate fuels were 63.35 and 52.35 wt%, respectively, compared to 47.81 and 36.58 wt% over unloaded USY zeolite. The characterizations of catalysts were studied and product distributions over different catalysts were presented and discussed. NiW/USY catalyst possessed higher acidity with good balance between strong and weak acid sites. NiW/USY catalyst also showed very good thermal stability.

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HYDROCRACKING OF PETROLEUM GAS OIL ON NiW/USY: EFFECT OF NICKEL AND TUNGSTEN CONTENT

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ABSTRACT

The effects of active component (tungsten) and promoter (nickel) content on surface structure and activity of NiW supported on Ultra-stable Y zeolite (USY) were studied in hydrocracking of petroleum gas oil in a high-pressure shaking reactor at reaction temperature of 450 °C, contact time of 90 minutes and catalyst to sample 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 concentration of nickel, the values of total conversion and yield of total distillate fuels were 64.35 and 54.12 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 68.71 and 51.38 wt%, respectively. The results of catalysts characterization using TGA-TPD acidity and TGA thermal stability were presented and discussed.

Keywords: Petroleum gas oil, USY-based catalyst, high-pressure shaking reactor.

INTRODUCTION

Hydrocracking 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. Hydrocracking process needs dual function catalysts, hydrogenation and cracking functions. Active component and promoters sulphides provide hydrogenation function, while supports provide the cracking functions. Active components are commonly transition metal sulphides of an element in group VIB (i.e. molybdenum (Mo) or tungsten (W)) that responsible for the principal chemical reaction. The active components saturate aromatics in the feed, saturate olefins formed in the cracking, and protect the catalyst from poisoning by the coke. A promoter is a chemical compound such as nickel (Ni) and cobalt (Co) which when added results in desirable activity, selectivity or stability effects. 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 (Kabe *et al.*, 1999). 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 liability of sulphur anions, thus leading to more numerous of active sites in the reductive atmospheric of the hydrotreating processes. Mijoin (1999) and Breysse *et al.*, (2001) 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 (Okamoto *et al.*, 2003).

Supports provide the cracking functions, 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 (Satterfield, 1993). 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 (Maesen *et. al*, 2004). USY zeolite was selected due to its superiority over other kinds of zeolites in hydrocracking reactions (Sato *et al.,* 1999). Zeolites are defined as crystalline aluminosilicates, have been investigated and extensively used in industry. Zeolites have been successful because of their crystallinity, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity. The elementary building units of zeolites are SiO_4 and AlO_4 tetrahedra. Among the properties which are affected by the framework alumina content are the density of negative framework charges, cation-exchange capacity, the density of Bronsted acid sites, their strength and thermal stability (Weitkamp, 2000). For the majority of catalytic applications, medium or large pore zeolites will usually be preferred. In the processes which work under hydrogen pressure, such as hydrocracking of heavy petroleum distillates, the catalytic activity stems from the Bronsted acid sites rather than the Lewis acid sites. It is well known, due to the higher electronegativity of silicon compared to alumina, the strongest Bronsted acid sites in zeolites will occur on completely isolated AlO_4-tetrahedra. This is the reason why, upon dealumination of Y-zeolites with typical Si/Al ratio of 2.5, the catalytic activity generally increase up to Si/Al ratio of 10. In this region, the gain in acid strength overcompensate the decrease in the density of Bronsted acid sites (Weitkamp, 2000).

This investigation concentrated on the effects of tungsten and nickel content on surface structure of NiW/USY in order to investigate its performance for hydrocracking of petroleum gas oil at reaction temperature of 450 °C, 90 minutes contact time and 0.04 catalyst to feed ratio. The catalysts characterizations were presented and discussed.

EXPERIMENTAL

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.

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 and °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 (Sato *et al.*1999, Hassan *et al.*2001). 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 (Ferrari *et al.*, 2001; Farag *et al.*, 1999).

The Experimental Set Up

The 70-ml stainless steel high-pressure shaking reactor was manufactured with 15.24 cm long and 2.21cm 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.

About 30 g of desulphurized petroleum gas oil (DS-GO) sample was firstly poured into the reactor, and then the catalyst was added in catalyst to 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 minutes 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 schematic diagram of the experimental set up is shown in Figure 1.

The conversion, product yield, and catalyst to 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 is 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.

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 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 (Ooi *et al.*, 2004, Tian *et al.*, 1998).

Gas Chromatograph (GC)

The gaseous products were analyzed using a gas chromatograph (Hewlett Packard, model No. 5890 series II) equipped with Porapak Q, 270cm-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.

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. 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 minutes. 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.

$$Acidity = \frac{W\left(\frac{1}{Mb}\right)\left(\frac{1000mg}{1g}\right)}{Wz} \qquad (4)$$

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

RESULTS AND DISCUSSION

TGA-TPD Acidity Measurements

The TPD profiles of NiW/USY catalyst with different tungsten and nickel concentrations are shown in Figures 2 and 3, respectively. The acid sites of NiW/USY catalyst carried out using temperature programmed desorption (TPD) was much more significant on all USY-based catalysts. 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. Although, the number of strong acid sites was higher at these tungsten and nickel contents and therefore consequently showed higher cracking activity than other catalysts.

Thermal Stability Analyzer (TGA)

TGA thermal gravity was used to carry out the stability of the catalysts. Figures 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 two stages of thermal decomposition behaviour of the catalysts: a plateau from 30 to 120 °C with a little weight loss due to the moisture release and a main weight of catalysts in the last stage. That means 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.

Product Distributions

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 minutes and catalyst to feed ratio of 0.04 using NiW/USY with different nickel and tungsten concentrations. These operating conditions used in the present investigation were selected according to the results obtained previously (Alsobaai *et al.*, 2006). Figure 6 presents the effect of tungsten concentration on conversion of gas oil at a constant nickel content of 5 wt%. For tungsten content less than 15 wt%, the total conversion and yields of all distilled products remained constant and other products (coke and gas) did not change. This means that the amount of active component (tungsten) not more enough to enhance the hydrogenation reactions. 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 68.71 and 51.38 wt%, respectively A maximum in activity is observed when the tungsten content reached 23 wt%, which corresponds to the present an enough amount of tungsten to a complete occupation of the edges of WS_2 slabs by the promoter.

Figure 7 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 64.35, 54.12, 11.09, 4.87, 38.16, 7.23 and 3.00 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.

CONCLUSIONS

The hydrocracking of petroleum gas oil in a high-pressure shaking reactor at reaction temperature of 450 °C, contact time of 90 minutes and catalyst to sample ratio of 0.04 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. 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 and maximum values of total conversion, yield of total distillate fuels, gasoline, kerosene, diesel gas and coke were 64.35, 54.12, 11.09, 4.87, 38.16, 7.23 and 3.00 wt%, respectively.

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

Zeolite type	USY
Commodity	HSZ-320NAA
SiO_2/Al_2O_3 mole ratio	5.5
Na_2O/Al_2O_3 mole ratio	1.00
X-ray crystallinity, %	101
Physical state	Solid
Solubility	Insoluble in water
Appearance	White powder

* Supplied by manufacture

Table 2 Distillation analysis of the gas oil

Temperature, °C	Volume, %
240	IBP
253	5
256	10
263	20
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279	50
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Table 3 Elemental composition analysis, wt % of the gas oil

C	85.17
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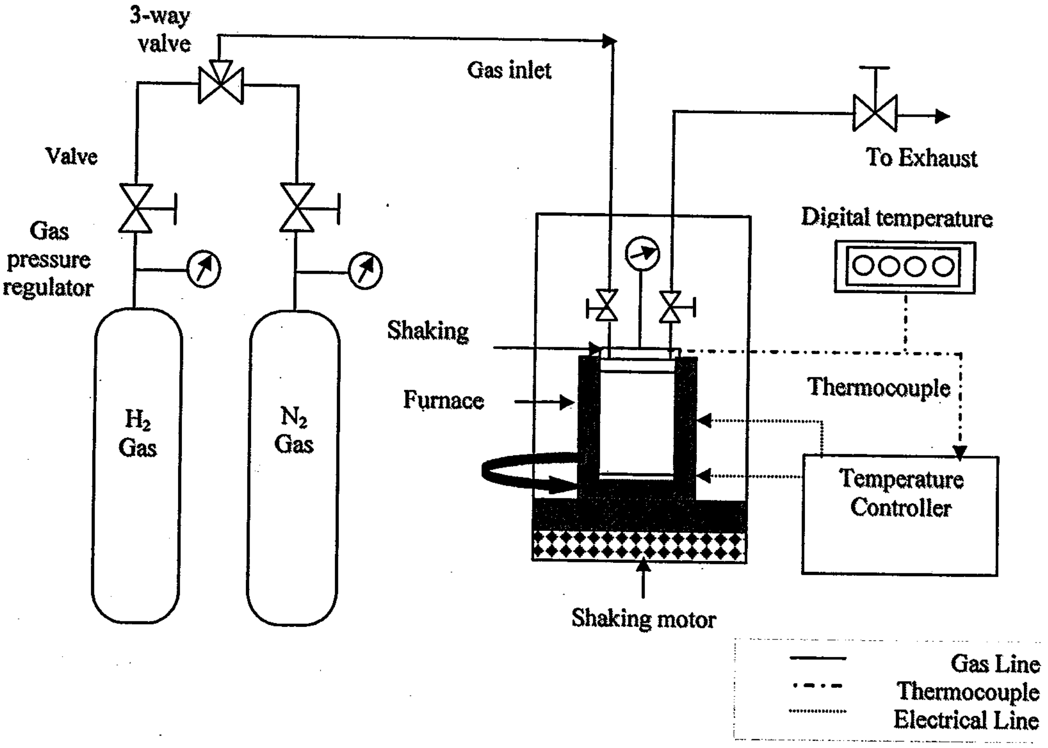

Figure 1 Schematic diagram of the experimental set up for hydrocracking of petroleum gas oil

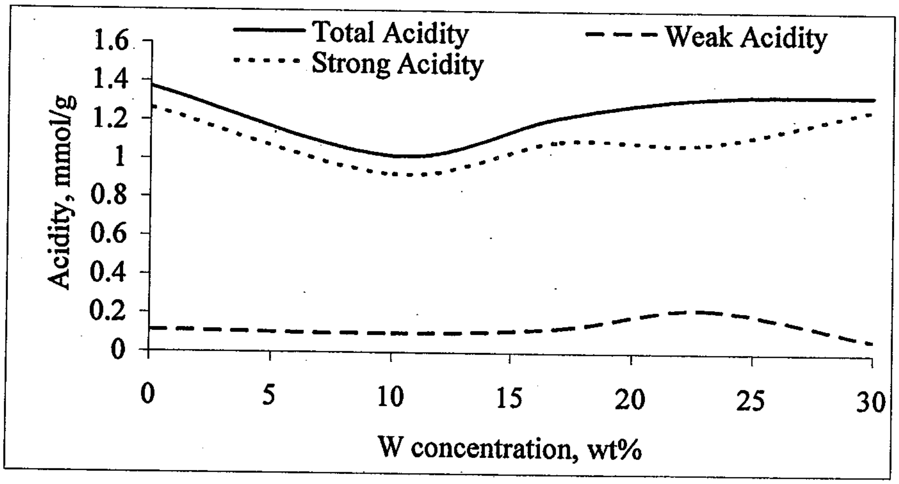

Figure 2 TGA-TPD acidity versus tungsten content

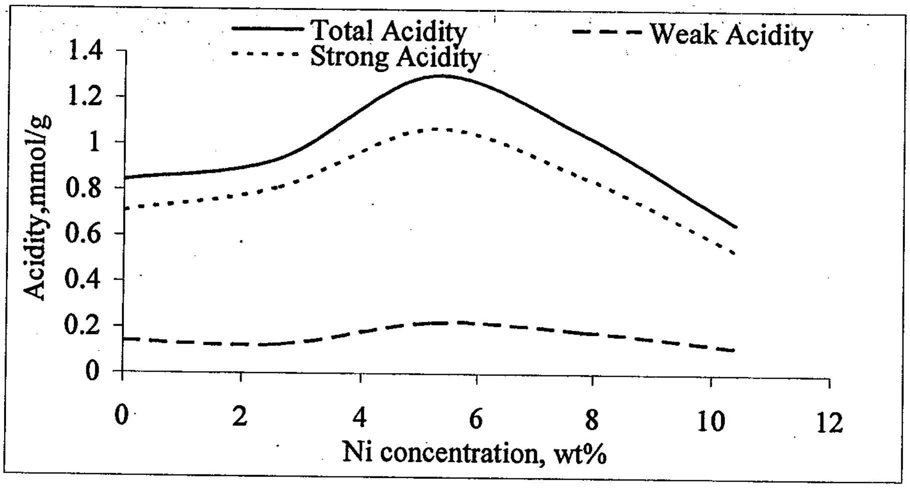

Figure 3 TGA-TPD acidity versus nickel content

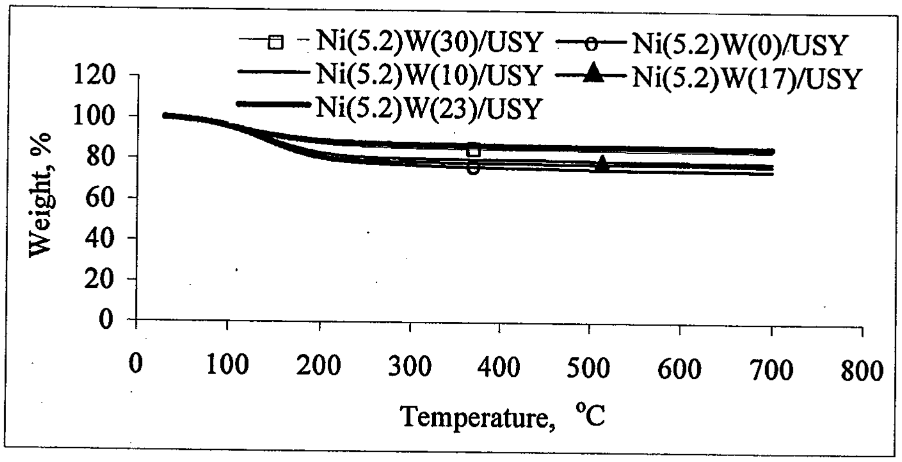

Figure 4 TGA thermal stability results for NiW/USY catalyst with different tungsten concentrations

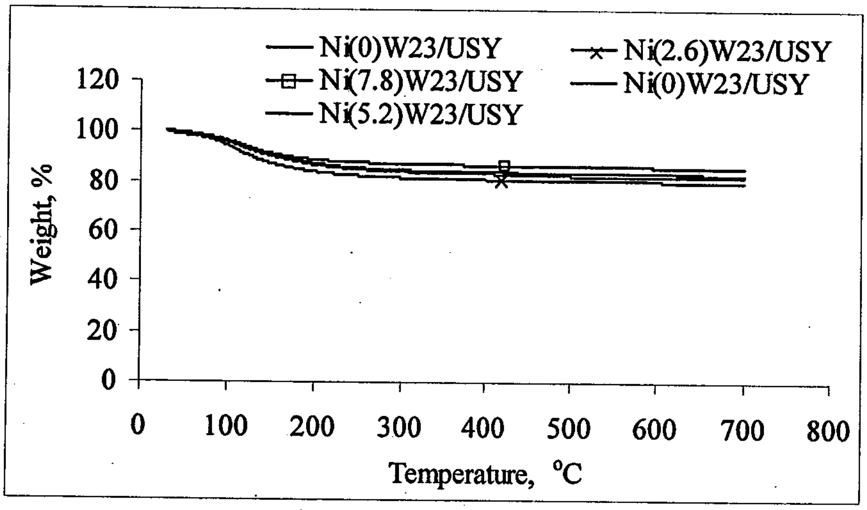

Figure 5 TGA thermal stability results for NiW/USY catalyst with different nickel concentrations

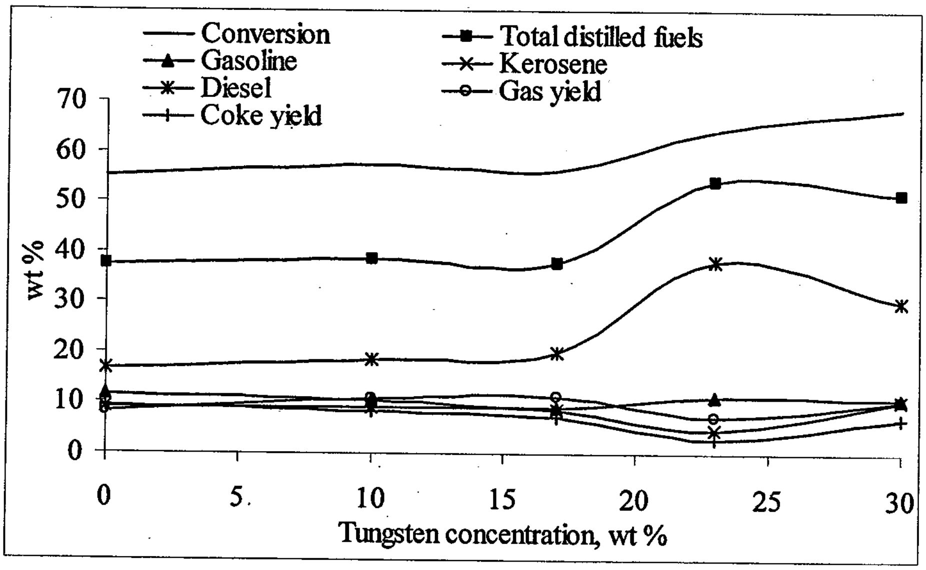

Figure 6 Gas oil conversion versus tungsten content

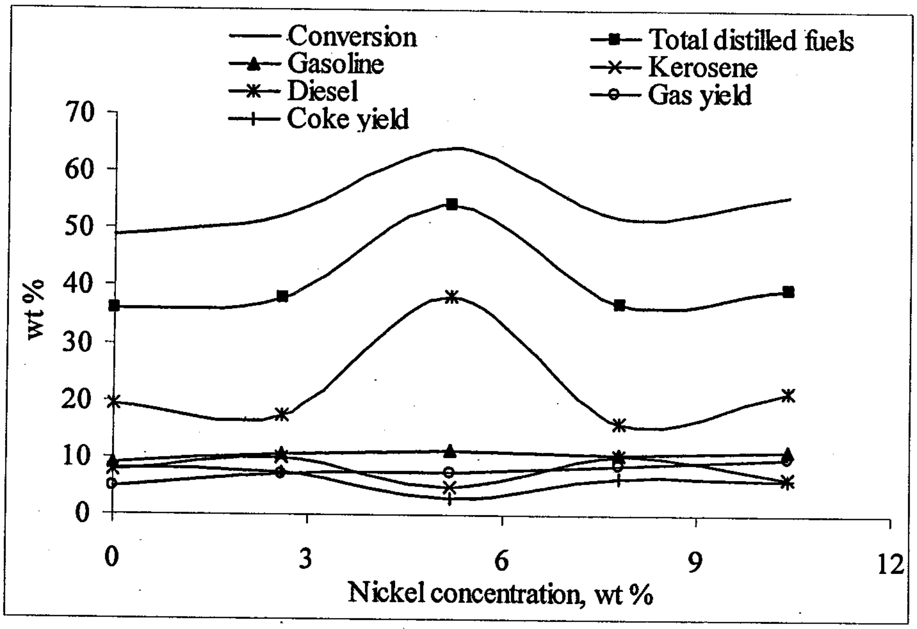

Figure 7 Gas oil conversion versus nickel content

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ACTIVITY AND CHARATERIZATION OF $NiMo/Al_2O_3$ HYDROCRACKING CATALYST

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Abstract *Catalytic activity of commercial nickel molybdenum supported on alumina catalyst ($NiMo/Al_2O_3$) was investigated in the hydrocracking of petroleum gas oil under various operating conditions, reaction temperature in range 300-450 °C, contact time 30-120 min and catalyst to gas oil ratio 0-0.08 using high-pressure shaking reactor. The product consists mainly from liquid, gas and coke. A total conversion of 59.61 wt% and a maximum value of 51.91 wt% of liquid product (total distillate fuels) were obtained at temperature of 450 °C, 90 minutes contact time and 0.04 catalyst to feed ratio. The catalyst was characterized by number of techniques and measurements, such as TPD-TGA acidity, TGA thermal stability, BET surface area, pore volume, pore size distribution, and SEM. Product distributions under different experimental conditions were presented and discussed.*

KEYWORDS: Petroleum gas oil, $NiMo/Al_2O_3$ catalyst, a high-pressure shaking reactor.

Introduction

Since total crude oil demand is projected to grow and the oil reserves in the world are limited, there is a strong need to convert hydrocarbon feed stocks into lower boiling point products in greater yields and with more selectivity. In many parts of the world, light oil production is declining and heavy oil conversion, therefore, becomes increasingly important to maintain economic viability of these regions (Heinrich *et al.*, 1997). Recently, the price of crude oil has reached US $ 72 per barrel in the international market (www.answers.com/topic/oil-price-increases-of-2005) and the majority of machines and equipments being made at present are designed to run using liquid fuel. Therefore, it is important to extract much useful materials from crude oil.

Many investigators have reported the production of light fuels from cracking of heavy oils over different cracking catalysts (Sato *et al.*, 1999). The catalysts used for the hydrocracking process are formed by composting various transition metals with the solid support such as alumina, silica, alumina-silica, magnesia, carbon and zeolites Speight (1998). Tian et al (1998) used batch reactor for the hydrocracking of residue oil over dispersed water-soluble Ni-Mo catalyst and alumina supported Co-Mo catalyst. The experiments were done under low operating conditions, hydrogen pressure of 7 MPa, temperature of 340 °C and time 30-240 min which suitable for this reaction. Absi-Halabi et al (1998) studied the performance of a Ni-Mo-W /γ-Al_2O_3 catalyst using Kuwait vacuum residue as feed. The results revealed that the Ni-Mo-W catalyst was more active than either the Ni-Mo or Ni-W catalysts. The effect of catalyst composition on desulfurization reaction showed that both the NiMo and mixed NiMoW catalysts have nearly the same activity pattern toward desulfurization. Kaluza and Zdrail (2001) reported MoO_3 activated carbon catalyst prepared by a new impregnation method for hydrodesulfurization process of thiophene. It was concluded that molybdenum trioxide was chemisorbed and highly dispersed 'monolayer ' form up to loading of about 15% MoO_3 and the almost levelled off. Sato *et al.* (1999) carried out the hydrocracking of tetralin over NiW/USY zeolite catalysts for improvement of heavy oil upgrading catalysts using a 50-ml batch type reactor at temperature of 250-400 °C, contact time of 3-180 min, catalyst loaded of 0.3 g operating pressure of 2-10.2 MPa. Their results revealed that the major reaction path in the initial period was found to differ from that later in the reaction. During the initial reaction period, tetralin is hydrocracked via a bimolecular process over both USY and NiW/USY. Subsequently, hydrocracking is catalyzed without the formation of heavy compounds.

Hydrocracking over NiW/USY is superior to that over USY only in the longer reactions. This difference is due to the limited role of NiW sulphide in the hydrocracking of tetralin. NiW sulphide hydrogenates aromatic compounds so that the cycloparaffinic compounds produced are easily cracked over acid sites.

The aims of this work are to investigate the effect of operating condition (temperature, reaction time and catalyst to feed ratio) on hydrocracking of petroleum gas oil over commercial NiMo/Al_2O_3 catalyst. Catalyst characterizations and Product distributions under different experimental conditions were presented and discussed.

Experimental

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 analyses of the gas oil are given in Tables 1 and 2. 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.

Table 1. 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 2. 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

Catalyst

Commercial NiMo/Al_2O_3 catalyst was provided by Sud-Chemie AG Germany. The chemical composition and physical properties of the NiMo/Al_2O_3 catalyst are listed in Table 3. The catalyst was supplied in 1.3 mm size and crushed to the size range of 75-125 µm. 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 (Ferrari *et al.*, 2001; Farag *et al.*, 1999).

Table 3. Chemical composition and physical properties of the $NiMo/Al_2O_3$ catalyst (Sud-Chemie AG Germany)

Property	Value
I. Chemical Composition (nominal)	
NiO, wt%	5.2 ± 0.5
MoO_3, wt%	23.0 ± 1.0
Na_2O, wt%	< 0.05
Al_2O_3, wt%	balance
II. Physical Properties (typical)	
Particle Shape, TRIAX-Shaped Extrusions	
Particle Size, mm	1.3
Bulk Density, kg/m^3	790
Surface Area, m^2/g	175
Pore Volume, l/kg	0.43
Side Crush Strength, N/kg	32
Loss of Attrition, wt. %	< 5

* Supplied by manufacture

The experimental set up

The 70-ml stainless steel high-pressure shaking reactor was manufactured with 15.24 cm long and 2.21cm 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.

About 30 g of desulphurized petroleum gas oil (DS-GO) sample was firstly poured into the reactor, and then the catalyst was added in different ratios from 0 to 0.08. Hydrogen valve was opened to develop a total hydrogen atmosphere after purging with nitrogen. The reactor was then heated to reaction temperature in the range 300-450 °C. The reaction was carried out for a fixed period of time in the range 30-120 minutes 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 schematic diagram of the experimental set up is shown in Figure 1.

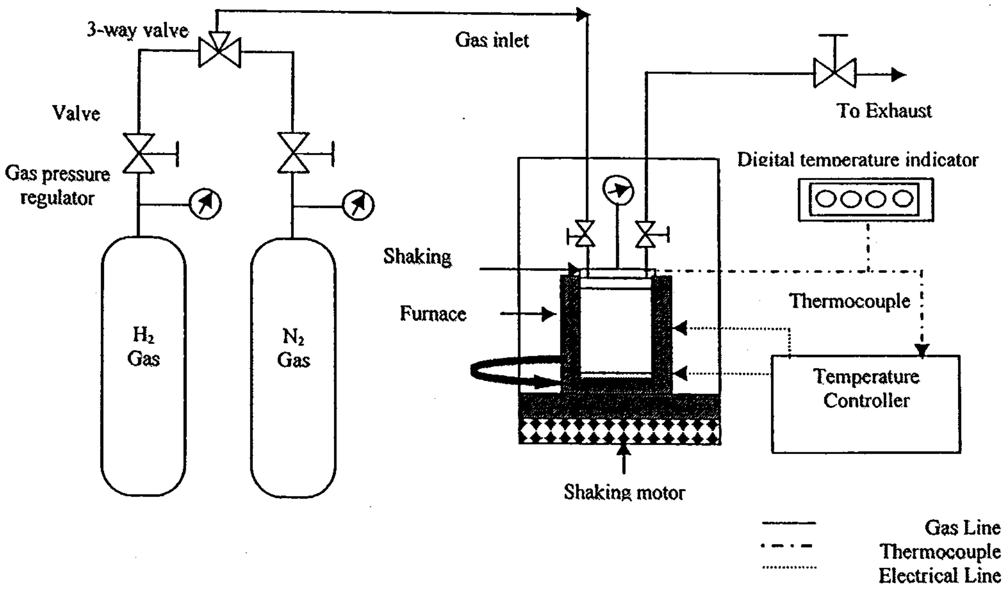

Figure 1. Schematic diagram of the experimental set up for hydrocracking of petroleum gas oil

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

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

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

$$Y_I = \frac{W_I}{W_{GO}} \times 100 \tag{2}$$

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

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

where W_{CA} is weight of catalyst loaded.

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 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 (Ooi *et al.*, 2004, Tian *et al.*, 1998).

Gas Chromatograph (GC)

The gaseous products were analyzed using a gas chromatograph (Hewlett Packard, model No. 5890 series II) equipped with Porapak Q, 270cm-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.

Nitrogen Adsorption

Pore volume, surface area and average pore diameter of synthesized catalysts were measured using Autosorb1, Quantachrome Autosorb Automated Gas Sorption System supplied by Quantachrome. The samples were degassed for 3 h under vacuum at temperature of 300 °C using Autosorb1 instrument before measurements were performed (Zhu *et al.*, 1999).

Scanning electron microscopy (SEM)

SEM studies were performed using Leica Cambridge Stereoscan 360, UK and Polaron for the coating system (sputter coating). SEM revealed quickly the normal size and shape of the particles, and providing a representative micrograph of the surface of supports and catalysts, and also to show the effect of metal on the particle size of supports. 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.

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. 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 minutes. 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.

$$Acidity = \frac{W\left(\frac{1}{Mb}\right)\left(\frac{1000mg}{1g}\right)}{Wz} \qquad (4)$$

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

Elemental analyser (EA)

The PE 2400 Series II CHNS Elemental Analyzer supplied by M/S Perkin Company, USA was used to determine H/C ratio and percentage of carbon, hydrogen, nitrogen and sulphur in the feed. About 1.5-2.5 mg of sample was put in a tin capsule unit. The maximum and minimum furnace temperatures were set at 975 and 500 °C. The required gases are highly purified helium, oxygen and compressed air.

Results and discussion

Catalyst characterization

The commercial NiMo/Al_2O_3 catalyst was characterized using different techniques. The BET surface area, pore volume and average pore diameter are given in Table 4 and the pore size distribution of this catalyst is shown in Figure 2. As evident from the Figure 2, alumina-based catalyst has mesopores which are desirable for the hydrocracking of heavy compounds.

Table 4. BET surface area, pore volume, average pore diameter and acidity of commercial NiMo/Al_2O_3 catalysts

BET surface area, m^2/g	175
Pore volume, cm^3/g	0.43
Average pore diameter, nm	9.8
Acidity, mmol /g_{Cat}	0.4228
Weak acidity, %	33.30
Strong acidity, %	66.70

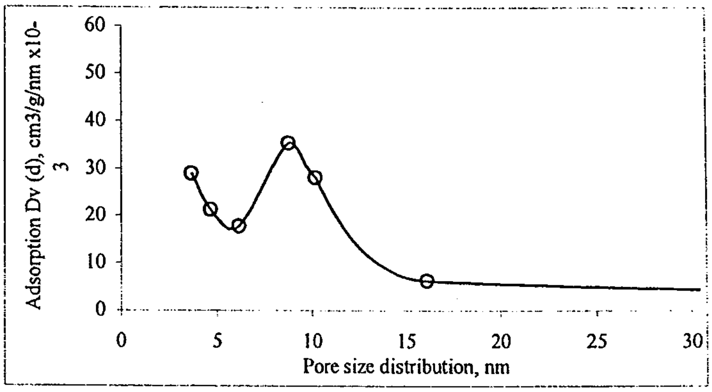

Figure 2. Pore size distribution of NiMo/Al_2O_3 catalyst

The acid sites of commercial NiMo/Al$_2$O$_3$ catalyst was carried out using TGA-TPD (temperature–programmed desorption). The number of weak and strong acid sites is presents in Table 4. The total number of acid sites, measured by the amount of isopropylamine, was 0.4228 mmol/g. The TGA-TPD profile is shown in Figure 3. The TGA-TPD measurements show that there are two acid sites, the peak in temperature range of 100-200 °C is associated to the weak acid site (weak Lewis type) and the second peak found in temperature range of 300-400 °C represents strong acid sites (strong Lewis type).

Thermal gravity experiment was carried out to study the stability of the catalyst. Figure 4 show the weight loss (TG) and DTG curves of commercial NiMo/Al$_2$O$_3$ catalyst. It can be seen two stages of thermal decomposition behaviour of the catalyst: a plateau from 30 to 120 °C with a little weight loss due to the moisture release and a main weight of catalyst in the last stage. That means the catalyst showed high thermal stability in the temperature range of 400-500 °C. This stability of the catalyst is favourable to prevent thermal decomposition of the catalyst during the reactions and regeneration processes.

Figures 5 show scanning electron microscopy of commercial NiMo/Al$_2$O$_3$ catalysts. It can be shown clearly the metals appear to be primarily randomly distributed although some aggregation could be detected.

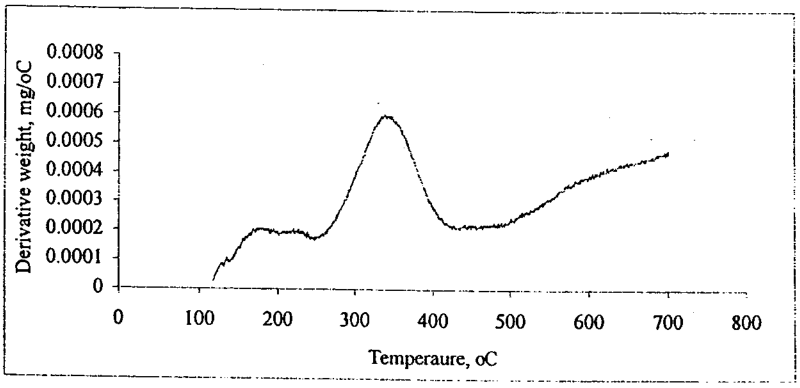

Figure 3. TGA-TPD acidity for NiMo/Al$_2$O$_3$ catalyst

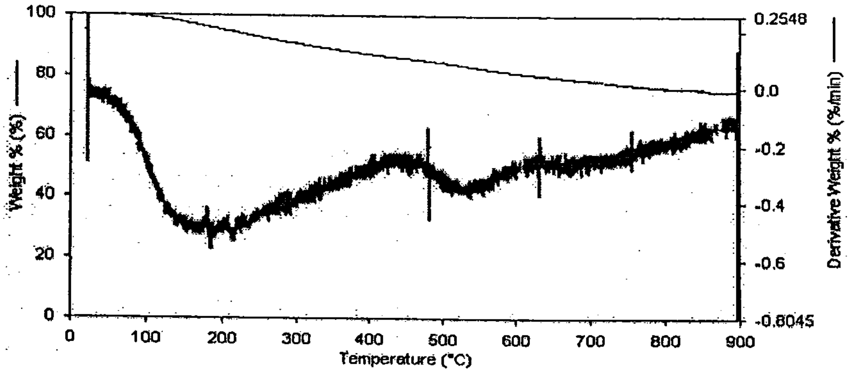

Figure 4. TGA result for commercial NiMo/Al$_2$O$_3$ catalyst

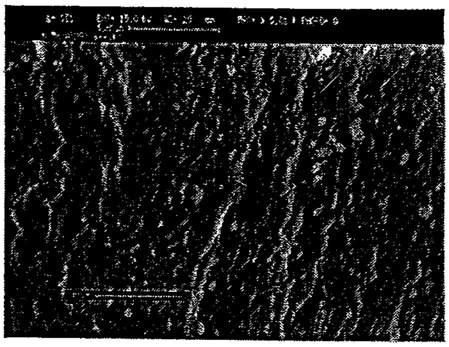

Figure 5. SEM images for NiMo/Al$_2$O$_3$ catalyst, magnification is 5000:1

Effect of reaction temperature

Table 5 shows effect of reaction temperature on the total conversion and products distribution over $NiMo/Al_2O_3$ at 120 minutes time and 0.04 catalyst to feed ratio. A total conversion of 58.24 wt% was obtained at temperature of 450 °C, while a minimum value of 14.50 wt% conversion was noticed at temperature of 300 °C. A maximum value of 47.54 wt% of liquid product (total distillate fuels) was obtained at 450 °C. The liquid product consists of gasoline, kerosene and diesel, where the yields of these products were 14.55, 14.42 and 18.57 wt%, respectively. Higher reaction temperature favours the hydrocracking reactions, which lead to formation gas, coke and liquid consists of higher percentage of the distillate fuels. At higher temperature, heavier compounds are cracked to product with lower boiling point. Usually at higher temperature more energy is provided to break the carbon-carbon bonds into shorter chains beside the action of the active catalyst that provide the active sites necessary for the cracking. Thus, the total conversion, distillate fuels were increased with increasing of the temperature. However, 10.70-wt% of both gas and coke were obtained under this temperature. Hence, the carbon-carbon bonds in liquid phase are cleaved to produce distillate fuels, gas and coke products, so these products and total conversion were found to increase with increasing reaction temperature.

Table 5. Gas oil conversion in the investigation of role of temperature range
(Conditions: Reaction time = 120 min, Catalyst to oil ratio = 0.04)

Temperature, °C	300	350	400	450
conversion	14.50	20.00	28.80	58.24
Total distilled fuels	11.20	17.00	22.70	47.54
Gasoline	-	-	0.86	14.55
Kerosene	-	0.98	2.54	14.42
Diesel	11.20	16.02	19.30	18.57
Gas + Coke	3.30	3.00	6.10	10.70

Effect of contact time

Table 6 presents effect of contact time on total conversion and yield of products at 450 °C temperature and 0.04 catalyst to feed ratio. It can be seen that total distillate products and diesel yield were increased with time until 90 minutes then decreased, while conversion and other wt% of distillate fuels were increased with reaction time. At lower reaction time, the complex compounds in gas oil were not completely cracked. The initial step in the hydrocracking of gas oil to lighter products involves free radical cracking (Gray, 1994). The free radicals and olefins resulting from this cracking are very reactive and can recombine to form heavy products. Stable oil and gas products resulting from primary cracking can also undergo free radical cracking and thus generate additional free radicals and olefins. These can further react to produce light and heavy products. The gas and coke products were constant with time until 90 minutes then increase. This increment of other wt% of distillate fuels at time above 90 minutes was happened because part of diesel product cracked to produce gasoline, kerosene, gas and coke products.

Table 6. Gas oil conversion in the investigation of role of contact time range
(Conditions: Reaction temperature = 450 °C , Catalyst to oil ratio = 0.04)

Time, min	30	60	90	120
Conversion	33.26	52.25	59.61	58.24
Total distilled fuels	31.26	49.95	51.91	47.54
Gasoline	6.33	8.54	10.00	14.55
Kerosene	4.84	5.48	8.47	14.42
Diesel	20.09	35.93	33.44	18.57
Gas + Coke	2.00	2.30	7.70	10.70

Effect of catalyst to feed ratio

Table 7 shows total conversion and yield of products as a function of catalyst to feed ratio at 450 °C reaction temperature and 90 minutes contact time. The total conversion was increased with catalyst to feed ratio and the maximum value of diesel and total distilled fuels was obtained at 0.04 ratio. The conversion and formation of distillate products are dominated by thermal cracking and the main role of catalyst is to enhance the uptake of hydrogen and prevent condensation and coking reactions (Gray, 1994). The hydrocracking reactions require significant breaking of carbon-carbon bonds. Breaking of C-C bonds relies on carbenium ion intermediates, promoted by the acid sites on the $NiMo/Al_2O_3$ catalyst surface.

Table 7. Gas oil conversion in the investigation of role of catalyst to feed ratio
(Conditions: Reaction temperature = 450 °C , Contact time = 90 minutes)

Catalyst to feed ratio	0	0.02	0.04	0.06	0.08
Conversion	36.70	39.15	59.61	58.91	59.65
Total distilled fuels	28.10	32.25	51.91	52.61	51.85
Gasoline	6.13	8.78	10.00	10.7	11.85
Kerosene	7.60	6.73	8.47	9.34	8.48
Diesel	14.37	16.74	33.44	32.57	31.42
Gas + Coke	8.60	6.90	7.70	6.30	7.80

Conclusions

The hydrocracking of petroleum gas oil at reaction temperature in range 300-450 °C, contact time 30-120 min and catalyst to feed ratio 0-0.08 was studied in high-pressure shaking reactor. Petroleum gas oil was converted to transportation fuels (gasoline, kerosene and diesel), gas and coke by hydrocracking over commercial NiMo/Al_2O_3 catalyst with total conversion of 59.61 wt% at temperature of 450 °C, 90 minutes contact time and 0.04 catalyst to feed ratio. The effect of different operating conditions on hydrocracking reaction over commercial NiMo/Al_2O_3 catalyst was studied and found that 450 °C reaction temperature, 90 min contact time and 0.04 catalyst to feed ratio are the most suitable operating conditions. Alumina-based catalyst showed very high thermal stability and has mesopores which are desirable for the hydrocracking of heavy compounds.

Acknowledgement

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Appendix D

Abstracts for Theses

DEVELOPMENT OF NEW ZEOLITE-BASED CATALYSIS FOR HYDROCRACKING OF GAS OIL : SYNTHESIS, CHARACTERIZATION, ACTIVITY AND KINETICS STUDIES

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2007

DEVELOPMENT OF NiW-ZEOLITE-BASED CATALYSTS FOR HYDROCRACKING OF GAS OIL: SYNTHESIS, CHARACTERIZATION, ACTIVITY AND KINETICS STUDIES

by

AHMED MUBARAK AHMED ALSOBAAI

Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

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PEMBANGUNAN MANGKIN BERASASKAN NiW-ZEOLIT UNTUK PERETAKANHIDRO MINYAK GAS: KAJIAN SINTESIS, PENCIRIAN, AKTIVITI DAN KINETIK

ABSTRAK

Satu reaktor goncang-bertekanan tinggi telah dibina untuk proses peretakanhidro bagi minyak gas dan kondisi pencampuran reaktor ini telah dikaji dalam penyelidikan ini. Peretakanhidro minyak gas telah dikaji keatas mangkin NiMo/Al_2O_3 pada suhu 300-450 °C, masa sentuh 30-120 min, nisbah berat mangkin kepada minyak gas 0-0.08 dan tekanan hidrogen 1000-3000kPa menggunakan reaktor goncang bertekanan tinggi. Nilai maksimum jumlah penukaran dan hasil bahan api sulingan adalah 59.61 dan 51.91%bt, masing-masing yang diperolehi pada suhu 450 °C, masa sentuh 90 min, nisbah mangkin kepada minyak gas 0.04 dan tekanan hidrogen 1000 kPa. Zeolit USY berasaskan NiMo, CoMo, NiW dan CoW disediakan menggunakan kaedah pengisitepuan basah. Keputusan ini menunjukkan mangkin NiW/USY memberikan jumlah penukaran dan hasil bahan api sulingan sebanyak 15.54 and 15.77wt%, masing-masing lebih tinggi daripada yang diperolehi daripada mangkin zeolit USY tanpa muatan. Mangkin NiW/USY dengan komposisi 5 %bt nikel dan 23 %bt tungsten memberikan jumlah penukaran dan hasil bahan api sulingan sebanyak 63.35 and 52.35 %bt, masing-masing. Suatu siri mangkin yang NiW berasaskan MCM-48 berliang meso dengan nisbah SiO_2/Al_2O_3 yang berbeza disediakan untuk mengkaji kesan kandungan alumina keatas sifat-sifat asid mangkin yang telah disintesis. Keputusan menunjukkan keaktifan dan sifat-sifat mangkin dapat diperbaiki dengan meningkatkan kandungan alumina dimana nilai maksima jumlah penukaran dan hasil bahan api sulingan yang diperolehi pada nisbah berat SiO_2/Al_2O_3 50. Bahan komposit MCM-48-USY juga disediakan dengan menyalut zeolit USY dengan satu lapisan bahan MCM-48 berliang meso pada nisbah SiO_2/USY yang berbeza digunakan sebagai penyokong untuk mangkin nikel dan tungsten. Keputusan menunjukkan nilai maksimum jumlah penukaran dan hasil bahan api sulingan adalah pada nisbah SiO_2/USY 0.5. Keputusan daripada tindakbalas peretakanhidro minyak gas menggunakan mangkin MCM-48-USY dibandingkan dengan keputusan yang diperolehi menggunakan mangkin USY dan MCM-48 yang digabungkan secara fizikal. Kinetik tindakbalas minyak gas menggunakan mangkin NiW/M50 juga dikaji. Mangkin-mangkin yang dipilih berasaskan keaktifan tindakbalas peretakanhidro, keasidan dan luas permukaan mangkin yang tinggi dengan purata saiz liang pada julat berliang meso yang amat bersesuaian untuk tindakbalas peretakanhidro minyak berat. Statistik rekabentuk ujikaji, (DOE), digunakan untuk memperolehi keadaan pengendalian optimum. Keputusan menunjukkan keadaan pengendalian optimum untuk peretakanhidro minyak gas oleh mangkin NiW/MCM-48 adalah pada suhu tindakbalas 465 °C, masa sentuh 30 min dan nisbah mangkin kepada minyak gas 0.05. Model kinetik "6-gumpal" yang mengandungi dua belas parameter kinetik telah dicadangkan untuk menerangkan tindakbalas peretakanhidro minyak gas. Keputusan juga menunjukkan hasil yang diperolehi dengan kaedah DOE adalah bersetuju dengan ujikaji yang dijalankan.

DEVELOPMENT OF NiW-ZEOLITE-BASED CATALYSTS FOR HYDROCRACKING OF GAS OIL: SYNTHESIS, CHARACTERIZATION, ACTIVITY AND KINETICS STUDIES

ABSTRACT

A high-pressure shaking reactor was fabricated for hydrocracking of gas oil and the mixing condition of this reactor was verified. The hydrocracking of gas oil was studied over NiMo/Al_2O_3 catalyst at reaction temperature of 300-450 °C, contact time 30-120 min, catalyst to gas oil ratio 0-0.08 and hydrogen pressure 1000-3000 kPa using high-pressure shaking reactor. Maximum values of total conversion and distillate fuels of 59.61 and 51.91 wt%, respectively, were obtained at temperature of 450 °C, 90 min contact time, 0.04 catalyst to gas oil ratio and1000 kPa hydrogen pressure. USY zeolite supported NiMo, CoMo, NiW and CoW were prepared using the incipient wetness method. Over NiW/USY catalyst, the total conversion and distillate fuels were 15.54 and 15.77 wt%, respectively higher than those obtained over unloaded USY zeolite. Then NiW/USY catalyst with different nickel and tungsten loadings were prepared. It was observed that at tungsten and nickel loadings of 23 and 5 wt%, the total conversion and yield of total distillate fuels were 63.35 and 52.35 wt%, respectively. A series of NiW supported on mesoporous MCM-48 with different SiO_2/Al_2O_3 ratios was prepared to study the effect of alumina on the acidic properties of synthesized catalysts. The catalyst activity and properties were improved with increasing alumina content and found that maximum values of total conversion and distillate fuels were obtained at SiO_2/Al_2O_3 ratio of 50. MCM-48-USY composite materials were also prepared by coating USY zeolite by a layer of MCM-48 mesoporous material at different SiO_2/USY ratios and used as support for nickel and tungsten catalysts. The maximum values of total conversion and distillate fuels were obtained at SiO_2/USY ratio of 0.5. The obtained results from hydrocracking of gas oil over composite MCM-48-USY catalysts were compared with those obtained over physically mixed USY and MCM-48 catalysts. The kinetic of gas oil was studied over NiW/M50 catalyst. This catalyst was chosen due to its high hydrocracking activity, acidity and surface area with average pore size in mesoporous range which is desirable for hydrocracking of heavy oil. Statistical design of experiment, (DOE), was used to obtain the optimum operating conditions. It was found that the optimum operating conditions for hydrocracking of gas oil over prepared NiW/MCM-48 catalyst are: reaction temperature of 465 °C, contact time of 30 min and catalyst to gas oil ratio of 0.05. A six-lump kinetic model contained twelve kinetic parameters was proposed to describe the hydrocracking of gas oil. It was found that the obtained results were in good agreement with those obtained from DOE and experimental results.

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HYDROCRACKING OF GAS OIL OVER ZEOLITE-BASED CATALYSTS

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Hydrocracking of gas oil over Zeolite-based catalysts.

Abstract

The objective of this work was to prepare USY/MCM-48 composite material as hydrocracking catalyst. Metal pairs Nickel and Tungsten were loaded on the composite material by co-impregnation using incipient wetness technique with content of 5.2 wt% of Nickel Oxide (NiO) and 23 wt% of Tungsten Oxide (WO_3). The catalyst produced posses high acidity and mesopores structure. The prepared catalyst was used to carry out hydrocracking of petroleum gas oil in a high pressure shaking reactor at reaction temperature of 440°C, 455°C, and 470°C contact time of 20, 40 and 60 minutes and catalyst to gas oil ratio of 0.04 at 20 bar hydrogen pressure. The products were collected and analyzed by ASTM and gas chromatography. The products consist of gas, gasoline, kerosene, diesel and coke. The highest conversion of each product were: gasoline 19.6% (470°C, 60 min), kerosene 12.9% (455°C, 60 min), diesel 28.8% (455°C, 60 min), gas 21.3% (470°C, 60 min) and total 78.9% (470°C, 60 min). The optimum temperature and reaction time was found to be 455°C and 60 minutes, respectively. Finally, kinetics study based on each temperature was done using lump model and the highest rate constant parameters were obtained at 455°C.

Keywords: Petroleum gas oil, Ultra-stable Y zeolite (USY), MCM-48, hydrocracking, gasoline, kerosene, diesel.

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