

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 SiO₂/Al₂O₃ 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.

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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 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 cetyltrimethylammonium 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 CTMAB: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 $[(\text{NH}_4)_{10}(\text{W}_{12}\text{O}_{41})]$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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-Elmer, 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 isopropylamine for 10 min. The desorption of physisorbed 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

$$\text{acidity} = \frac{W(\text{g})(1/M_b(\text{mg}/\text{mmol}))(1000 \text{ mg}/1 \text{ g})}{W_Z(\text{g})} \quad (1)$$

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 $20 \text{ cm}^3/\text{min}$ from ambient temperature to 110°C with a control heating rate of $20^\circ\text{C}/\text{min}$. 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 $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at 40 kV and 30 mA and scanning speed of $2^\circ/\text{min}$.

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:

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

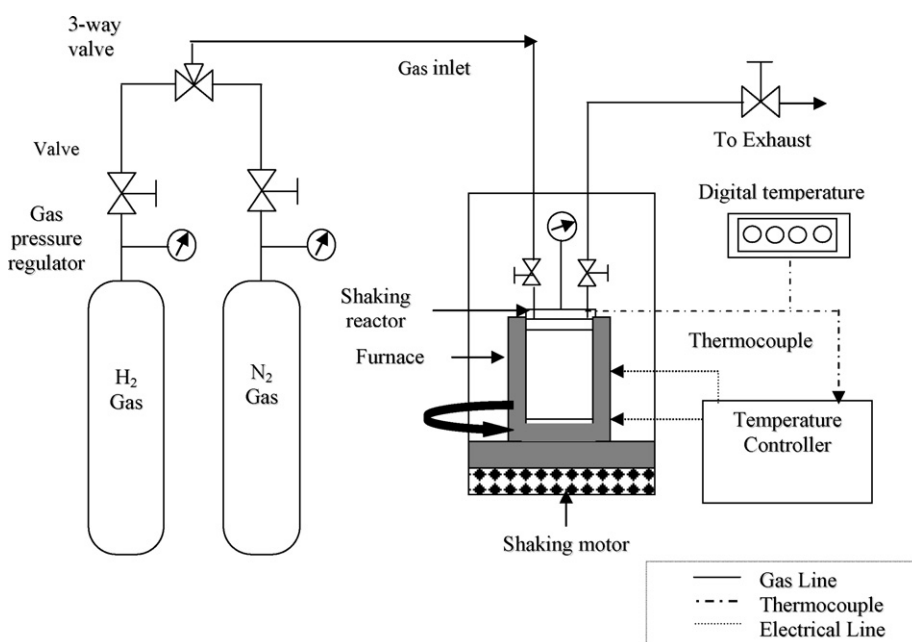


Fig. 1. Schematic diagram of the experimental setup for hydrocracking of petroleum gas oil.

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

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

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.

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

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 \times 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)

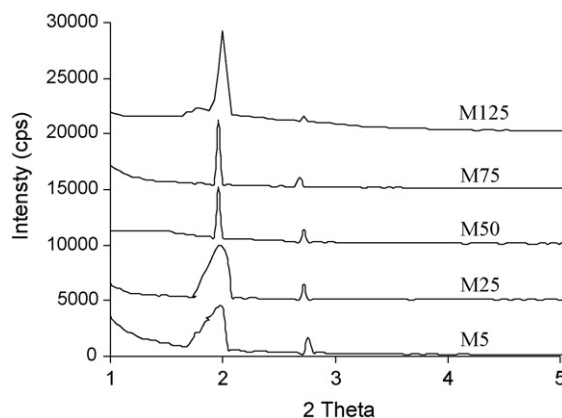


Fig. 2. XRD pattern for mesoporous molecular sieve MCM-48 with different SiO_2/Al_2O_3 ratio.

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 mesoporous 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.

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

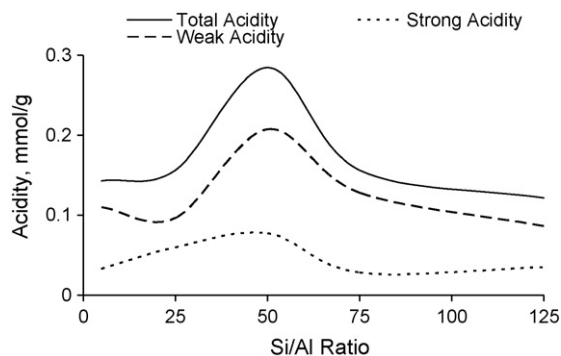


Fig. 3. TGA-TPD acidity for MCM-48 supports vs. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

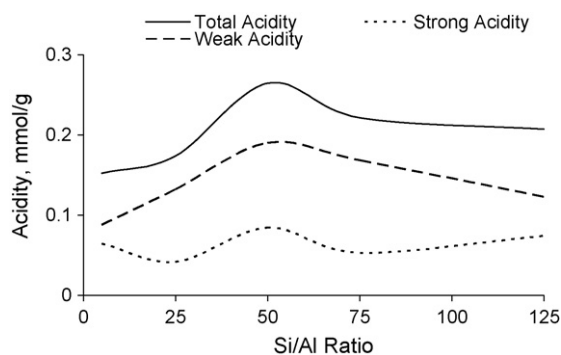


Fig. 4. TGA-TPD acidity for NiW/MCM-48 catalysts vs. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

with Al content until $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 50 then decreased. The incorporation of Al into the framework generated acid sites which were able to interact with the base. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of prepared samples presented in Table 1 indicated that alumina was present in the solid framework. The higher ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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

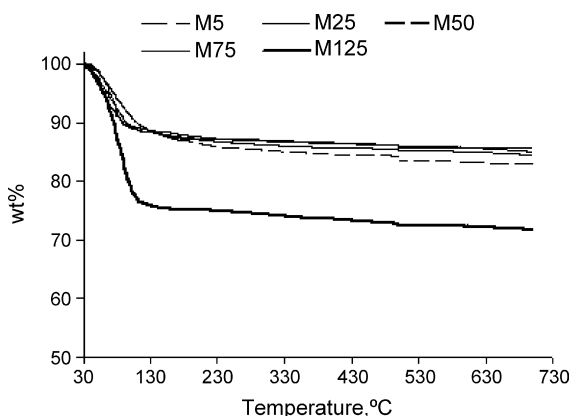


Fig. 5. TGA thermal stability results for MCM-48 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

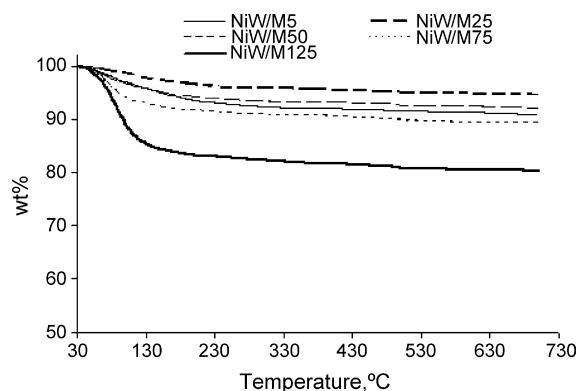


Fig. 6. TGA thermal stability results for NiW/MCM-48 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

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.

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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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

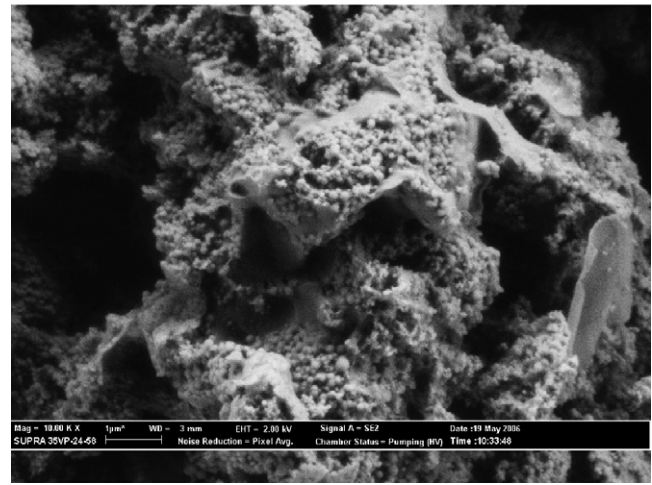
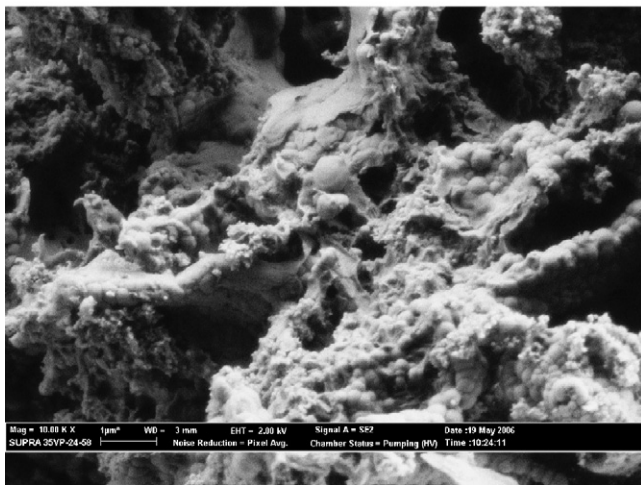
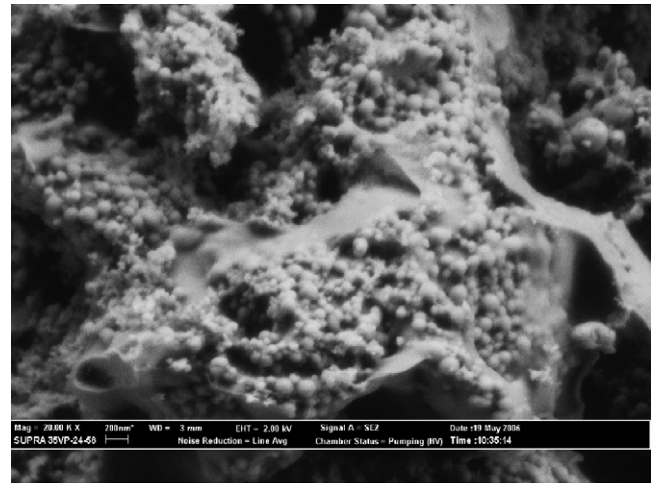
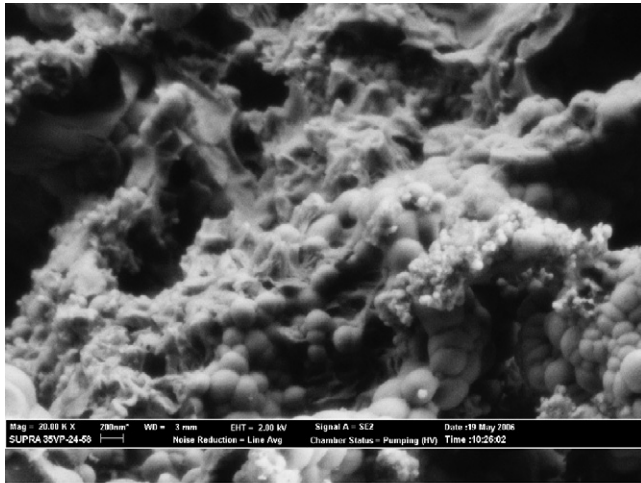


Fig. 7. Scanning electron micrographs of M50 support.

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 hydrocracking over MCM-48 with different SiO₂/Al₂O₃ 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 ₂ H ₄	0.57	0.27	0.32	0.25	0.25
C ₂ H ₆	22.94	52.65	22.70	25.43	36.59
C ₃ H ₆	5.43	1.58	3.40	2.32	2.18
C ₃ H ₈	21.42	27.23	34.68	28.34	34.15
C ₄ H 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

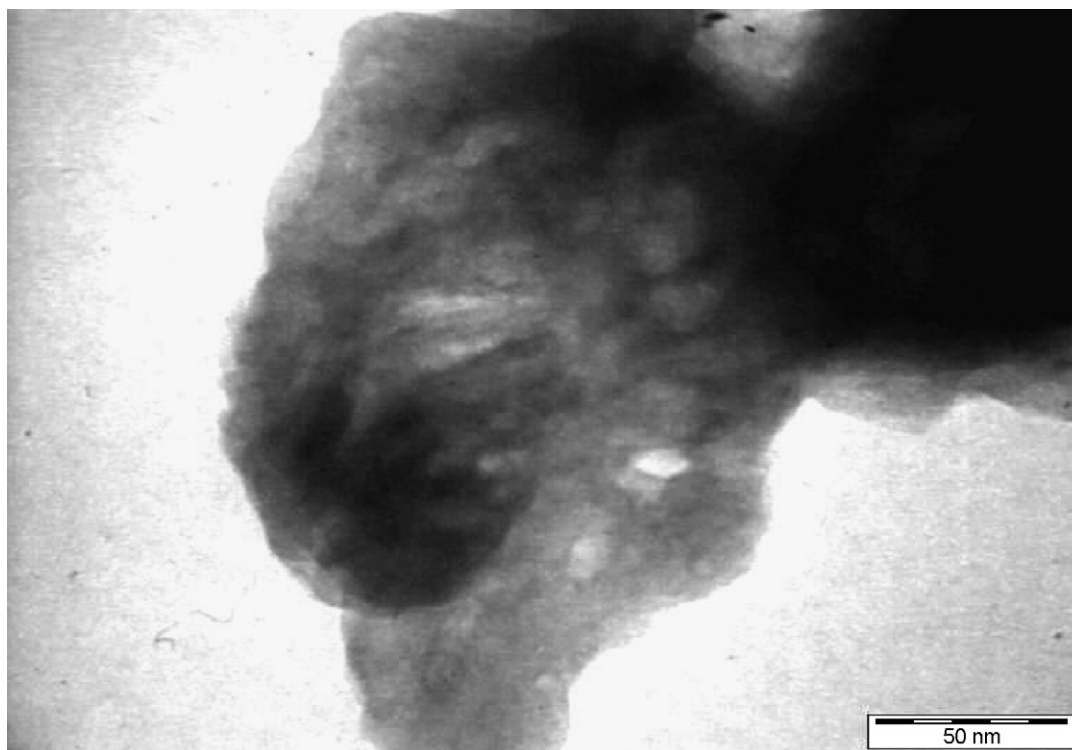


Fig. 9. TEM images of NiW/MCM-48 with SiO₂/Al₂O₃ ratio of 50.

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 SiO₂/Al₂O₃ ratio till SiO₂/Al₂O₃ ratio of 50 then decreased. The acidity and porosity of catalysts

influenced the product distribution obtained from the catalytic hydrocracking. NiW/MCM-48 with SiO₂/Al₂O₃ 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 SiO₂/Al₂O₃ ratio. This confirms the role of the strength of acid sites on the cracking reaction. Catalysts prepared with low

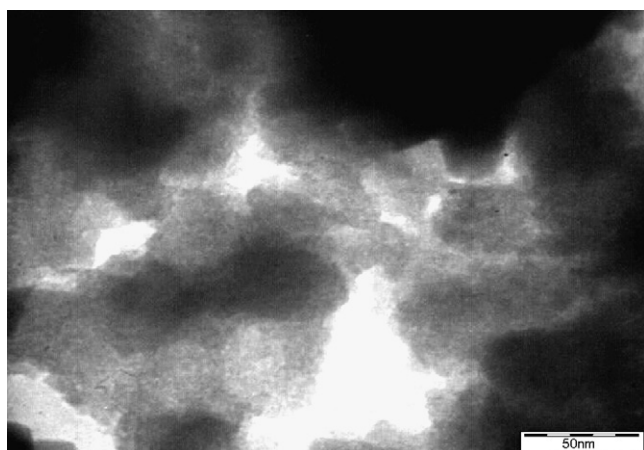


Fig. 10. TEM images of NiW/MCM-48 with SiO₂/Al₂O₃ ratio of 75.

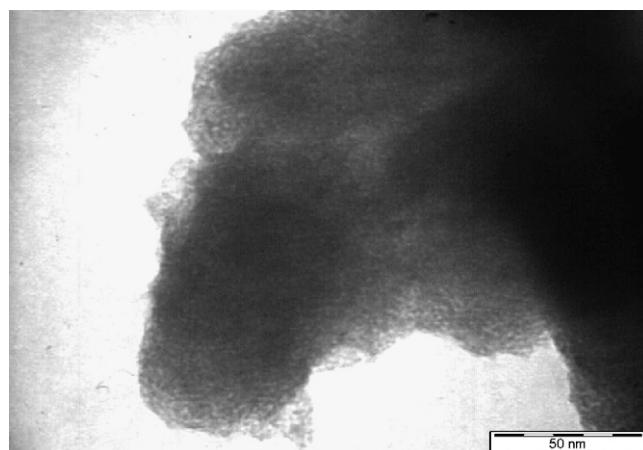


Fig. 11. TEM images of NiW/MCM-48 with SiO₂/Al₂O₃ ratio of 125.

Table 5
Gas oil hydrocracking over NiW/MCM-48 with different SiO₂/Al₂O₃ 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 ₂ H ₄	0.20	0.27	0.16	0.29	0.20
C ₂ H ₆	51.95	51.65	42.08	46.32	47.52
C ₃ H ₆	1.42	1.58	1.32	1.63	2.88
C ₃ H ₈	29.69	27.23	34.03	30.09	30.73
C ₄ H 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

SiO₂/Al₂O₃ 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

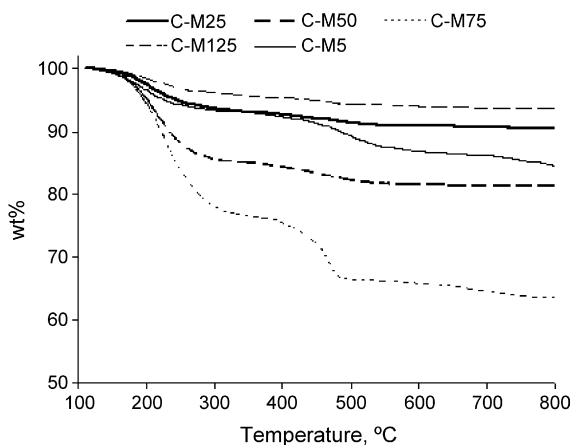


Fig. 12. Profiles of weight loss with temperature of coked MCM-48 with different SiO₂/Al₂O₃ ratio.

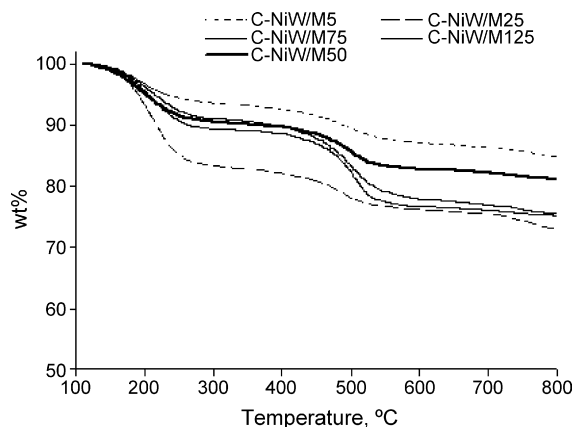


Fig. 13. Profiles of weight loss with temperature of coked NiW/MCM-48 with different SiO₂/Al₂O₃ ratio.

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.

4. Conclusions

In summary, mesoporous molecular sieve MCM-48 with different SiO₂/Al₂O₃ 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 SiO₂/Al₂O₃ ratios (5, 25, 50, 75, 125) catalysts, NiW/MCM-48 with SiO₂/Al₂O₃ of 50 (NiW/M50) exhibited better catalytic activity for gas oil hydrocracking.

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