Modified mesoporous HMS supported Ni for deoxygenation of triolein into hydrocarbon-biofuel production

Suraya Zulkeplia, Joon Ching Juana,⁎, Hwei Voon Leea, Noor Saadah Abd. Rahmanb, Pau Loke Showc, Eng Poh Ngd

a Nanotechnology & Catalysis Research Centre, University of Malaya, 50603 Kuala Lumpur, Malaysia
b Department of Chemistry, Faculty of Science Building, University of Malaya, 50603 Kuala Lumpur, Malaysia
c Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor Darul Ehsan, Malaysia
d School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM Penang, Malaysia

ARTICLE INFO

Keywords:
Nickel
Mesoporous HMS
Deoxygenation
Hydrocarbons
Biofuel

ABSTRACT

A series of modified hexagonal mesoporous silica (HMS) supported by various Ni loading (5 wt% Ni, 10 wt% Ni, 40 wt% Ni and 100 wt% Ni) have been synthesized and systematically characterized. The resultant Ni catalysts improved the performance of the deoxygenation (DO) of triolein at a reaction temperature of 380 °C in a simple glass batch reactor under a solvent-free condition and are hydrogen-free. The incorporation of Ni loading into the HMS framework caused the catalytic activity to increase when compared to that of HMS. Surprisingly, 10 wt% Ni loading was highly dispersed on the HMS which is capable of achieving 92.5% and 95.2% of conversion and selectivity, respectively. This is due to the synergistic effect of Si-O-Ni bonding and high dispersion of NiO on HMS. In this respect, the nature of catalyst support such as pore size and the high surface areas of HMS play an important role in enhancing the catalytic performance of DO reaction. This study has revealed that Ni/HMS catalyst is a promising catalyst that can be applied to the development of sustainable biofuel from non-edible oil.

1. Introduction

The growing need for renewable fuel production, coupled with the quickly dwindling availability of fossil fuels has widened the research interest in search of the renewable energy sources for the manufacture of chemicals and hydrocarbon fuels [1–17]. Hence, the development of renewable energy is growing increasingly attractive to many researchers due to the abundance of renewable resources [4,10,18,19]. Moreover, there are various renewable energy sources usually found on Earth, including biomass, solar, wind, and nuclear sources, which can substitute fossil fuels [12,20–25]. More importantly, the consumption of renewable energy is a potential mechanism for the growth of economic, industrial, and agricultural sectors, domestic needs, and transportation to serve fundamental needs of human beings [9,18,22,26–29]. However, these renewable energy sources have inevitably generated several problems during its handling, associated with the disposal of waste and radioactive pollution, derived from biomass and nuclear energy respectively [21,30,31]. In addition, wind, as well as solar energy, is restricted by the surrounding environment due to high cost and environmental concerns, thereby deterring their applications [32,33]. Therefore, biomass energy has been recognized to be the most promising renewable energy source in the transportation sector.

Natural plant oil, also known as triglycerides, consists of C8–C24 fatty acids [34]. This biomass is derived from triglycerides-based plant oils (obtained from palm oil, microalgae, jatropha plants, cottonseed, canola, peanut, sunflower oils, fat from animal sources and used cooking oil), which have been utilized for biofuel production [4,6,8,9,15,19,28,35–40]. Such natural oil sources contain high viscosity, low volatility and high amounts of unsaturated acids, which have generated several problems in engine application, such as injector coking, carbon deposits, sticky oil rings, lubricant thickening and similar problems [18,36]. However, the natural plant oil is currently not cost competitive when compared to the mainstream petrochemical industry due to the large use of raw material and production costs [28,41]. Many efforts have been tried to elevate alternative sources of renewable energy to replace biodiesel by finding new technology for clean, renewable fuel [27,42,43]. Zeolites have been used for the
cracking of triglycerides to eliminate oxygen moieties, but it has caused the loss of a significant portion of carbon and energy [44]. According to previous reports, the most conventional technology for biodiesel synthesis is by using the transesterification technique, which utilizes triglycerides in the incidence of a solvent and homogeneous acid/base catalyst to produce fatty acid methyl esters (FAME) [4,35,39,45–53]. However, this technique leads to the formation of soap by saponification, thus resulting in catalyst deactivation [45,54–56]. These unfavorable methods are linked to filter plugging, the reason metal components become corroded, and the formation of residue on fuel pumps in the presence of alkaline or acidic catalysts due to the high content of oxygen atoms in biodiesel [18,57–60]. Therefore, this biodiesel is not entirely compatible with a diesel engine.

Alternatively, the oxygen in the plant oil can be eliminated via deoxygenation (DO), which undergoes the decarboxylation (−CO2) and decarbonylation (−CO) processes [34,49,61]. Catalytic deoxygenation (DO) has been developed to produce green hydrocarbon based biofuel in the absence of H2 efficiently, by eliminating oxygenated compounds from the plant oil in the form of CO, CO2, or H2O over solid acids or base catalysts [34,62–64]. Therefore, various metal catalysts have been synthesized for DO of natural triglycerides under elevated H2 pressure and temperature such as Pd, Ni, and Co, which are commercially supported (e.g.: HZSM-5, HBet, ZrO2, CeO2, SiO2, TiO2, Al2O3, SiO2-Al2O3, and carbons) [17,63–66]. It was reported that biofuel is frequently used in the presence of H2 which is called hydrodeoxygenation (HDO). Unfortunately, the usage of H2 in a DO reaction is inefficient because of its costly reactor, storage difficulties, and transportation issues [63,67].

Therefore, it is very important that deoxygenation can be achieved without the consumption of H2 for biofuel production. Despite its potent reaction to noble metals (e.g., Pd and Pt), supported by activated carbons which have been tested in deoxygenation of triglycerides under inert gas or atmospheric conditions, its application may be restricted due to its exorbitant cost and scarcity [63,68–70].

More recently, Kordulis and co-workers (2016) reviewed the application of Ni over a variety of catalyst supports on the adaptation of triglycerides and associated model compounds as green diesel [17]. It was reported that the conversion of triolein was performed at 350 °C under an inert gas atmosphere for 6 h with 46.8% selectivity of C8–C17 [65]. Similarly, 20 wt% Ni supported on carbon was tested for deoxygenation of tristearin at 360 °C in the presence of H2 for 6 h with 77% selectivity of C4–C17 [66]. This clearly demonstrates that Ni-based catalysts are used in most DO reactions due to their cost-effectiveness, availability, and superior activity [57,71]. Nevertheless, the DO catalytic activity is still insufficient in comparison to Ni catalysts because of the longer reaction time in the presence of the additional gas [65,66]. Thus, numerous researchers have tailored new catalyst support and improved conditions through the deoxygenation of plant oil into hydrocarbon-fuel with better activity and greater selectivity than those that are being currently applied.

Several mesoporous catalyst supports (e.g., SBA-15, HBEA, HZSM-5, SAPO-11) have been customized for the deoxygenation of triglycerides [17,72]. Compared to microporous support (e.g., zeolite), it has a smaller pore size (pores < 20 Å), which leads to limited access to active sites of catalyst surfaces, thus diminishing the catalytic ability [55,73–75]. Therefore, mesoporous silica catalyst support have been considered for deoxygenation, owing to their promising chemical and textural properties which are as follows: (1) large surface areas (−1000 m2/g) [76,77], (2) greater textural mesoporosity [78], (3) flexible large pore size (−40 Å) [79], (4) strong-weak acidity, (5) higher thermal stability (up to 1073 K) [74], as well as (6) a high adsorption for hydrocarbon storage with strong resistance to deactivation which favors cracking in the triglycerides [17,56,76,79]. Hence, recent researchers have shown interests in the development of mesoporous HMS due to the catalyst being environment-friendly, robust and industrially feasible because inexpensive chemical reagents have been applied in the synthesis. Interestingly, the extraordinary advantages of mesoporous HMS have resulted in the continuous application of mesoporous HMS in various catalytic transformations which include photocatalysis [80,81], drug delivery devices [82], Fisher-Tropsch synthesis [83,84], hydrotreating [85], benzylization of benzene [86] and hydrodechlorination of chlorobenzene [87]. HMS has emerged as a universal catalyst support for chemical reactions with large molecules based plant oil due to the high diffusion on the catalyst surface, thereby enhancing catalytic processes [73,88–90]. Mesoporosity plays an essential role in the catalysis that includes liquid-phase reaction [75,91]. Moreover, the addition of Ni metal into HMS has promoted hydrogenation or dehydrogenation reaction for facilitating the deoxygenation pathway. In this respect, the chemical nature of the HMS used for Ni catalysts plays a crucial role in their catalytic activity which favors acidity in the cracking-deoxygenation.

In the present work, the researchers are focused on a series of Ni supported HMS in the DO of triolein to produce a green hydrocarbon-fuel in the absence of H2 and solvent. Triolein was selected as a representative of the triglyceride’s model compound due to its structural similarity with the plant oil, as it is composed of three oleic acids. The researchers have yet to find a study about the deoxygenation of triolein over HMS supported Ni catalysts at 380 °C for 2 h, to investigate the performance of Ni supported on HMS. In addition, the relationship between the physicochemical properties of Ni/HMS catalyst and the catalytic performances of DO are discussed.

2. Experimental

2.1. Materials

The chemical compounds applied in this synthesis were tetraethyl orthosilicate (TEOS; 98%) and dodecylamine (DA; 98%), which were purchased from Sigma-Aldrich. Nickel Nitrate hexahydrate (Ni (NO3)2•6H2O; ≥99.0–101.0 wt%) was obtained from Merck.

The chemical solvents such as Hexane (98%) and Ethanol (EtOH, 95%) were bought from Merck. Distilled water was used throughout this study.

Carbon supports were also commercially purchased from Sigma-Aldrich. All the chemicals were analytical standard and can be used devoid of any additional purification.

2.2. Preparation of catalysts

2.2.1. Synthesis of pure hexagonal mesoporous silica (HMS)

The pure hexagonal mesoporous silica (HMS) was synthesized according to a modified procedure via a neutral templating pathway (S° P°), using the dodecylamine (DDA) as a structure directing agent (S°) and the silica source (P°) used was tetraethyl orthosilicate (TEOS) [92]. The molar ratio of HMS synthesis was 1.0TEOS: 0.28DDA: 7EtOH: 128H2O. To prepare the mesoporous HMS, DDA acted as the organic linkers to the mixture of EtOH/H2O to improve the solubility process (S° P°). A vigorously stirred solution of the surfactant mixture of EtOH/H2O (10/90, v/v), and TEOS solution was added dropwise to the homogenous mixture obtained. Stirring was done to the mixture over a period of 24 h at room temperature before aging it for 6 h to encourage a higher amount of silica crosslinking [93]. The white product obtained was filtered and washed three times with distilled water until the pH solution 7 was obtained. After that, the sample was dried overnight at 100 °C. The template of HMS was removed by calcination in air at 580 °C for 6 h with the ramping rate of 10 °C/min. This catalyst support was designated as HMS.

2.2.2. Synthesis of Nickel-supported on hexagonal mesoporous silica (Ni/HMS)

A series of Ni/HMS catalysts were synthesized with 5, 10, 40 and 100 wt% Ni contents and they were supported on HMS as catalyst.
support via an incipient wetness impregnation technique. The aqueous solution of Ni(NO₃)₂·6H₂O was subsequently loaded onto the HMS support for 24 h and was further dried at 120 °C for 24 h and then calcined at 600 °C for 5 h in a muffle furnace. After calcination, all the Ni/HMS catalyst samples were grounded into a fine powder before use. The catalyst was denoted as xNi/HMS in which x is the weight percent (wt%) of Ni.

2.3. Characterization of catalysts

An XRD analysis was executed on a Bruker AXS D8 Advance by means of Cu kα (wavelength, λ = 1.542 Å) at 40 kV to identify the phases present in the NiO supported on HMS and the crystallinity of NiO using Scherrer’s equation. The sample was mounted on the sample holder and then inserted into the XRD diffractometer. The XRD data was documented in the 2θ range of 1.5° to 80° with a scanning speed of 0.6 deg min⁻¹, a step size of 0.04° for a step time of 1 s. The XRD data file was interpreted using the X’pert high score plus software. The characterization of the NiO phases was determined according to the JCPDS data library and simultaneously matched to those previously reported regarding the NiO catalysts. However, the pure NiO was used as a comparison with the other NiO impregnated over hexagonal mesoporous silica (HMS). Thus, the appropriate NiO peaks were confirmed in the XRD diffractograms.

The morphology of the surface and the atomic composition of the nickel upon impregnation on mesoporous HMS catalyst were determined using the field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX) after the samples were coated with platinum. The elemental and chemical mapping analysis were used to identify the dissemination of metal species after impregnation.

The images of Ni onto the silica surface were recorded by a high-resolution transmission electron microscopy (HR-TEM, Model: JEM 2100-F) operating at 200 kV of accelerating voltage. Prior to the analysis, the samples were disseminated in absolute ethanol by stirring with an ultrasonic bath and finally deposited onto a lacey carbon grid. The samples were dried in an oven for a few hours. HR-TEM and elemental mapping analysis were used to identify the particle size dissemination images of the Ni/HMS catalysts and its dispersion on HMS support respectively.

The surface area and porosity of the catalysts were analyzed with the TriStar II 3020 using low temperature N₂ physisorption isotherms. Before carrying out the analysis, the samples were degassed at a ramping rate of 10.0 °C/min to 350 °C to remove the physisorbed water immediately. Then, the samples were evacuated at temperatures of 90 °C and held for 60 min. After 1 h, the samples were heated at 350 °C for 8 h. The samples were chilled and then backfilled with N₂ gas. The analysis was made to determine the specific surface in the relative pressure range of 0.05–0.3. The total pore volumes were governed based on how much nitrogen was adsorbed at relative pressure (P/Po) of ca. 0.99. The pore size was determined by the Barrett–Joyner–Halenda (BJH) method.

FT-IR analysis was performed on a FT-IR Bruker Vertex 80/80v spectrometer to identify the surface of a functional group of HMS pure silica catalysts and to study the modification of Ni doped on the HMS silica catalyst. The FT-IR data was recorded from 4000 to 400 cm⁻¹ using the KBR pellet method.

Raman analysis was measured to identify the molecular nature of the nickel supported on the mesoporous HMS materials by Renishaw InVia Raman Microscope, using 325.0 nm Ar⁺ laser radiation. The excitation laser was concentrated on a circular spot of about 2 μm in diameter. The resolution was 4 cm⁻¹, and 1000 scans were documented for every spectrum.

The acidity of the catalysts was analyzed by temperature programmed desorption of ammonium (NH₃-TPD) (Thermo Finnigan TPD/R/O1100) equipped with a thermal conductivity detector (TCD). The acidity of the catalysts was studied using NH₃ as a probe molecule. In a typical experiment, 0.05 g of the catalyst was left under N₂ gas flow for 30 min at 250 °C. Following this, the catalyst was exposed to the NH₃ gas for 60 min at ambient temperature to facilitate the adsorption of NH₃ on the surfaces. The remaining NH₃ was subsequently removed by flowing N₂ gas before the analysis. TCD identified the desorption of the NH₃ from the acid sites of the catalyst under helium gas (30 mL/min) ranging from 50 °C to 900 °C. The TPD curve was identified by measuring the area under the curve with the total acidity of the catalyst to distinguish the acid strength from its NH₃ desorption profile.

2.4. Deoxygenation of triolein

The catalytic deoxygenation of triolein was executed in a 100 mL reactor, equipped with a digital heating mantle with a magnetic stirrer, a thermometer, a chiller and a vacuum reactor. In this experiment, 0.5 g of Ni/HMS catalysts and 10.0 g triolein were placed in a reactor, as shown in Fig. 1. Then, the reactor was linked to the vacuum line for
30 min to flush out the air prior to DO reaction. The temperature was heated up to 380 °C and was maintained for 2 h. After several mins, the vapour becomes condensed as it passes through the condenser, which was fitted in the middle of the flask. The condensed hydrocarbon liquid product was collected for GC–MS analysis. The experiment was conducted three times to ensure the validity of the results.

2.5 Product analysis

The liquid hydrocarbon-biofuel product was quantitatively analyzed using GCMSQP2010 Plus Shimadzu coupled with a mass spectrometer (MS), flame ionization detector (FID) and a thermal conductivity detector (TCD). The RTX 5 MS column (30.0 m × 0.25 µm × 0.25 mm) was also used. In the meantime, the internal standard of 1-bromohexane was prepared for quantitative analysis. Prior to analysis, each sample was diluted with n-hexane to 600 ppm. An aliquot of 1 µl of sample was inserted into the GCMS column. The liquid product was analyzed according to the standard hydrocarbon solution of C8–C20 by comparing the retention time. The temperature in the GC oven was set from 40 to 300 °C and the oven temperature was programmed at 40 °C and kept for 36.9 kPa. The oven temperature was programmed at 40 °C and kept for 2 min, then increased to 300 °C at a ramping rate of 5 mL/min and held for 40 min.

The performance of the catalyst was studied by the deoxygenation ability in terms of conversion (X %) according to the Eq. (1) [94]. The conversion is defined as the actual amount of reactants reacting to other products (e.g., liquid, gas) upon deoxygenation.

Conversion (X %) = \[ \frac{\text{Initial mass of reactants} - \text{Final mass of reactants after reaction}}{\text{Initial mass of reactants}} \times 100\% \] (1)

Based on the GCMS analysis, the composition of hydrocarbon in the liquid product mainly consists of alkane and alkene ranging from C6 to C20. The identity of the hydrocarbon fraction in the GC chromatogram was interpreted according to the standard mass spectra from the National Institute of Standards and Testing’s (NIST) library [95,96]. According to existing literature [62,63,95,97], the peak area from the GC chromatogram is proportional to the relative percentage of the hydrocarbon product. Therefore, the selectivity of the organic liquid product (SOLP %) was evaluated using Eq. (2) [94,98], by determining the desired chemical compounds such as carboxylic acid, alcohol, cycloalkane, alkenes and alkanes hydrocarbons (C6–C20), heavy hydrocarbons (> C20) and the sum of all the observed area products upon deoxygenation.

Selectivity of the product (SOLP %) = \[ \frac{\text{Total area of desired organic compounds (Cn)}}{\text{Total area of the product (n)}} \times 100\% \] (2)

The selectivity of hydrocarbon (S,) was calculated as the ratio of the desired carbon atoms to the total area of hydrocarbon (Cn–C20), which was given as Eq. (3):

Selectivity of hydrocarbon (S, %) = \[ \frac{\text{Area of the hydrocarbon fraction (Cn)}}{\text{Total area of hydrocarbons (n)}} \times 100\% \] (3)

3. Results and discussion

3.1 Characterisation of catalyst

3.1.1 X-ray diffraction (XRD) analysis

The XRD diffractogram shows the phase identification of the mesoporous HMS and HMS supported Ni catalysts at a low angle and a wide-angle depicted in Fig. 2. The typical characteristic peak of the mesoporous HMS is at 2θ = 1.80° with a wormhole structure which corresponds to the (1 0 0) plane of hexagonal mesoporous silica [87]. However, the diffraction of the HMS peak decreases as follows: HMS > 5 wt% Ni/HMS > 10 wt% Ni/HMS > 40 wt% Ni/HMS. These results show that the mesoporous HMS structure slightly deteriorates upon the impregnation of NiO [72]. Furthermore, a broad hump near to 2θ = 20° was observed at a wide-angle, indicating the presence of non-crystalline SiO2 in the mesoporous HMS [86]. On the other hand, the diffraction peaks of Ni/HMS catalysts at 2θ = 37.3°, 43.3°, 62.9° and 75.4° are attributed to the face-centred cubic structured NiO characteristics, corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) lattice planes (JCPDS Card No: 47-1049) respectively [99,100] (Fig. 2). Remarkably, these results confirm that the diffraction peaks of 100 wt% Ni catalyst are higher than other catalysts, which show that 100 wt% Ni (NiO) is mainly composed of large crystallite sizes. In fact, it has been reported that the sharpness of diffraction peaks significantly increase with an increase in particle size [101]. In contrast to 5–40 wt% Ni/HMS catalysts, the intensity of the NiO peaks became slightly reduced with the incorporation of Ni into HMS framework. Nevertheless, as the Ni loading increases, the poor distribution of NiO is formed on the HMS support. Table 1 summarizes the crystallite sizes of NiO phases, which are calculated by Scherrer’s equation. The result shows that the crystallite size of NiO (2 0 0) phase increases about twofold, from 16.2 nm (5 wt% Ni) to 38.8 nm (100 wt% Ni) (Table 1). This phenomenon might be related to the weak interactions between Ni and the HMS support, leading to the significant amount of aggregation in the pore wall of the HMS surfaces. Furthermore, as the diffraction peak of (1 0 0) decreases, the crystallinity of mesoporous HMS is reduced upon the introduction of NiO on HMS (Fig. 2).

3.1.2 Field-emission scanning electron microscopy (FESEM-EDX) with elemental mapping analysis

The morphology of the pure HMS and Ni/HMS catalysts are

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average crystallite sizes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO phase (1 1 1)</td>
<td>NiO phase (2 0 0)</td>
</tr>
<tr>
<td>HMS</td>
<td>27.8</td>
</tr>
<tr>
<td>5 wt% Ni/HMS</td>
<td>42.7</td>
</tr>
<tr>
<td>10 wt% Ni/HMS</td>
<td>30.5</td>
</tr>
<tr>
<td>40 wt% Ni/HMS</td>
<td>47.3</td>
</tr>
</tbody>
</table>

Fig. 2. Low angle XRD (right) and wide-angle (left) XRD patterns for calcined (a) HMS, (b) 5 wt% Ni/HMS, (c) 10 wt% Ni/HMS, (d) 40 wt% Ni/HMS and (e) 100 wt% Ni catalysts in the domain of 1.5–80° (2θ).
It is observed that the pure HMS consists of irregular spherical structures, with a significant level of particle sizes (average particle size $\sim 150$–$500$ nm) (Fig. 3(a)) [102–104]. On the other hand, 5 wt% Ni/HMS show that some HMS particles are aggregated. Hence, the Ni species are not well-distributed over the HMS surface according to the elemental mapping of 5 wt% Ni/HMS catalysts, as shown in Fig. 4. However, the 10 wt% Ni/HMS catalyst reveal that the small irregular clusters of Ni species are attached to the surface of the HMS support, which still retains the structure of the HMS surfaces. While for the 40 wt% Ni/HMS catalyst, some particles are agglomerated, which are then slightly cracked into smaller spherical sizes due to the high loading of 40 wt% Ni (Fig. 3(d)). The FESEM image of 100 wt% Ni show that the large NiO particles are composed of sharp-edged cubic shapes.

Furthermore, the Ni/HMS catalysts were subjected to FESEM-EDX with elemental mapping (EDS) analysis to confirm the dissemination of the metal species inside the catalysts as depicted in Fig. 4. It is observed that the presence of Ni, Si and O species are dispersed over the surface of HMS upon impregnation. Furthermore, the actual loading of 5 wt% Ni, 10 wt% Ni, 40 wt% Ni and 100 wt% Ni on the HMS contain 4.54 wt % Ni, 11.02 wt% Ni, 39.50 wt% and 100 wt% Ni respectively (Table 2). Eventually, this result shows the experiment on Ni loading is relatively presented in (Fig. 3(a)–(d)). It is observed that the pure HMS consists of irregular spherical structures, with a significant level of particle sizes (average particle size $\sim 150$–$500$ nm) (Fig. 3(a)) [102–104]. On the other hand, 5 wt% Ni/HMS show that some HMS particles are aggregated. Hence, the Ni species are not well-distributed over the HMS surface according to the elemental mapping of 5 wt% Ni/HMS catalysts, as shown in Fig. 4. However, the 10 wt% Ni/HMS catalyst reveal that the small irregular clusters of Ni species are attached to the surface of the HMS support, which still retains the structure of the HMS surfaces. While for the 40 wt% Ni/HMS catalyst, some particles are agglomerated, which are then slightly cracked into smaller spherical sizes due to the high loading of 40 wt% Ni (Fig. 3(d)). The FESEM image of 100 wt% Ni show that the large NiO particles are composed of sharp-edged cubic shapes.

Furthermore, the Ni/HMS catalysts were subjected to FESEM-EDX with elemental mapping (EDS) analysis to confirm the dissemination of the metal species inside the catalysts as depicted in Fig. 4. It is observed that the presence of Ni, Si and O species are dispersed over the surface of HMS upon impregnation. Furthermore, the actual loading of 5 wt% Ni, 10 wt% Ni, 40 wt% Ni and 100 wt% Ni on the HMS contain 4.54 wt % Ni, 11.02 wt% Ni, 39.50 wt% and 100 wt% Ni respectively (Table 2). Eventually, this result shows the experiment on Ni loading is relatively
similar to its theoretical value. It is worth mentioning that Ni was successfully incorporated into the mesoporous HMS.

3.1.3. High-resolution transmission electron microscopy (HR-TEM) analysis

Fig. 5 shows a representative of HR-TEM micrograph to determine the size of Ni particles and Ni distribution over mesoporous HMS. It is observed that some agglomeration of HMS sphere shapes are in the range of 150–500 nm in particle sizes. Also, the typical HMS looks like a wormhole-like mesopores structure (Fig. 5(b)), which is similar to the report by Pinnavia and co-workers [102]. The black Ni particles are shown in the TEM images. The black Ni particles are distributed over the HMS surface when the Ni/HMS catalysts are tested. It is important to note that the size of Ni particles increases with increasing Ni loadings (5–40 wt%) upon impregnation over the HMS support. Hence, the scattering of Ni is relatively non-uniform as illustrated in Fig. 5. This is because NiO may have a lower dispersion rate due to excessive Ni loading over the HMS. This contrasts with the 100 wt% Ni catalyst (Fig. 5(f)), which shows a large distribution of NiO particle sizes (average particle size ~ 360–460 nm), which plays a favorable role in deoxygenation DO).

3.1.4. Brunauer-Emmett-Teller (BET) analysis

The textural parameter of the HMS creates no conflict with the corresponding NiO support on the HMS catalysts, which is summarized in Table 2. The newly synthesized pure hexagonal mesoporous silica (HMS) shows the highest specific surface of 915 m²/g and the largest pore volume of 1.20 cm³/g. This result indicates that the newly developed mesoporous HMS has been synthesized as a catalyst support, which plays a major role in the DO of triolein. Meanwhile, the surface areas of the 5, 10, 40 wt% Ni loading is supported by HMS and bulk NiO are 432, 515, 334 and 1.59 m²/g respectively (Table 2). It is observed that the surface area of Ni which is supported by HMS has significantly dropped with the increase of 40 wt% Ni loading into the HMS framework upon impregnation [87]. A high NiO loading on HMS may reduce the silica network strength and connectivity, resulting in smaller pore sizes, and a significant decrease in surface area (Table 2). However, the pore volume of HMS catalyst has slightly reduced from 1.20 to 0.79 cm³/g upon impregnation with Ni. On the contrary, the pore sizes of the Ni/HMS catalyst (6.97 nm) gradually grew bigger than pure HMS 4.32 (HMS) upon impregnation. The increased pore size is mainly due to the enlargement of pore walls during surface modification. As shown in Table 2, the surface areas of 5 wt% Ni/HMS (S₂BET = 432 m²/g) become slightly decreased compared to that of 10 wt% Ni/HMS (S₂BET =

---

**Table 2**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area S₂BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
<th>Metal content (wt.%)</th>
<th>Total of acid (µmol of NH₃·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMS</td>
<td>915</td>
<td>1.20</td>
<td>4.32</td>
<td>–</td>
<td>471</td>
</tr>
<tr>
<td>5 wt% Ni/HMS</td>
<td>432</td>
<td>0.79</td>
<td>6.97</td>
<td>11.02</td>
<td>578</td>
</tr>
<tr>
<td>10 wt% Ni/HMS</td>
<td>512</td>
<td>0.76</td>
<td>5.39</td>
<td>11.02</td>
<td>1537</td>
</tr>
<tr>
<td>40 wt% Ni/HMS</td>
<td>334</td>
<td>0.54</td>
<td>4.65</td>
<td>39.50</td>
<td>1157</td>
</tr>
<tr>
<td>100 wt% Ni</td>
<td>1.59</td>
<td>0.03</td>
<td>–</td>
<td>100</td>
<td>545</td>
</tr>
</tbody>
</table>

*a* Surface areas was determined by BET analysis.

*b,c* Pore volume and pore size were determined by BJH method.

*d* Metal content was calculated from EDX analysis.

*e* Acidity was determined by TPD-NH₃ analysis.
Based on the SEM image (Fig. 3), the HMS particles after being deposited with 10 wt% Ni loading are much better preserved compared to that of 5 wt% Ni loading. Consequently, 10 wt% Ni/HMS possesses a larger surface which is also observed from the nitrogen isotherm (Fig. 6). A possible explanation for this phenomenon is that the bulk of NiO is separated from HMS, and thus HMS is better preserved.

The N2 adsorption–desorption isotherms of pure HMS and the subsequent NiO catalysts are displayed in Fig. 6. According to the IUPAC classification, the pure HMS and the corresponding NiO supported by HMS exhibit a standard type of isotherm IV with H1-type hysteresis loop, which indicates the presence of textural mesoporous materials [105]. This result is in agreement with the XRD analysis of mesoporous HMS (Fig. 2). In fact, the hysteresis loop is linked with the shape and the pore sizes of the HMS and Ni/HMS catalysts. Likewise, in this study, the large hysteresis loop of pure HMS is observed to be at a relative pressure of $0.40 \leq P/P_0 \leq 1.00$ due to the water-rich system (water: ethanol) 90:10 (v/v) during the synthesis of HMS silica. Indeed, the mesoporosity of HMS plays a significant role in the catalytic activity because it can improve the performance of large molecules such as triglycerides. It is noticeable that the small hysteresis loop of HMS at a relative pressure of $0.50 \leq P/P_0 \leq 0.90$ has reduced after being impregnated with 5 wt% of Ni loading. Therefore, it is proposed that some NiO crystallites are clogging the mouths of smaller pores in HMS, leading to an enlargement of the pore sizes from 4.32 to 6.97 nm. However, the pore volume indicates a reduction (see Table 2) from 1.20 to 0.79 cm$^3$/g. It is also reported elsewhere [106] that these results are possibly due to the substitution of Ni, which leads to a slight contraction of pore walls of HMS which can also be seen from the XRD pattern (low angle) in Fig. 2. The peak at [100] becomes broader and weaker under higher loading which indicates the collapse of the pore walls. The N2 adsorption–desorption of 100 wt% Ni catalyst is a typical type of
isotherm type III without the hysteresis loops, which shows that NiO has a characteristic of non-porous solids [87]. The 100 wt% Ni (NiO) catalyst is prepared to be compared with NiO supported by HMS catalysts.

3.1.5. Fourier transform infrared (FTIR) analysis

The FTIR spectra of the pure HMS, Ni/HMS catalysts, and the possible bond formation between Ni and HMS (SiO₂) is investigated (Fig. 7). Typically in HMS, the silica has four absorption bands which are located in the midinfrared region (1400–400 cm⁻¹), including Si–O–Si asymmetric stretching at ~1084 cm⁻¹, assigned to the tetrahedral SiO₄ structural units, Si–OH stretching vibrations at ~960 cm⁻¹, Si–O asymmetric stretching mode at about 800 cm⁻¹, and Si–O bending mode at ~470 cm⁻¹ from the tetrahedral sites.

Fig. 6. N₂ adsorption-desorption of isotherm of (a) HMS, (b) 5 wt% Ni/HMS, (c) 10 wt% Ni/HMS, (d) 40 wt% Ni/HMS and (e) 100 wt% Ni.
could be due to the higher adsorption of vibrational energy by the NiO absorption band at 581 cm$^{-1}$ (Fig. 8(b)). However, the absorption band at $\sim$960 cm$^{-1}$ is slightly reduced after being impregnated with NiO, which suggests that the interaction of Si–OH with NiO has occurred. These results are in accordance with the previous results [93,109,110]. The broad peak at $\sim$1650 cm$^{-1}$ is assigned to the bending vibration of adsorbed water bands [71,111]. The band at $\sim$3475 cm$^{-1}$ corresponds to the OH stretching vibrations of silanol (Si–OH) groups deposited at the external surface of the mesoporous material [112]. Therefore, this band decreases slightly with the increase of NiO into the HMS framework. This result indicates that the interaction between the surface Si–OH and Ni species may be present in the structure of HMS after the loading of Ni is saturated [113]. Sidik et al. (2015) and Setiabudi et al. (2017) also found that the decrease of $\sim$3475 cm$^{-1}$ as the metal loading increases is due to the formation of Si–O–Ni bonds in the Ni/MSN catalysts [113,114]. It is important to note that the intensity of the absorption band at $\sim$1084 cm$^{-1}$ decreases gradually with an increase in Ni loading due to the interaction of Si–O–Si with Ni to form a new band of Si–O–Ni bonds [111,115]. Therefore, it can be concluded that the Ni species are partially coordinated with the Si–OH group and may also result in the new type of Lewis and Bronsted acid sites. A similar observation is also reported by other researchers [111,113,116].

3.1.6. RAMAN analysis

Fig. 8 shows the Raman spectrum of mesoporous HMS after being impregnated with various amounts of Ni. As expected, there is no absorption peak for the HMS samples (Fig. 8(a)). This phenomenon is similar to the amorphous silica due to the presence of fluorescent interference and low sensitivity toward silica [115]. In Fig. 8(b)–(e), an intense peak at $\sim$1118 cm$^{-1}$ is observed after being deposited with Ni, and thus this peak is assigned to the Ni–O asymmetric stretching mode [88,117–120]. The two weaker peaks at $\sim$717 cm$^{-1}$ and $\sim$897 cm$^{-1}$ are assigned to the internal and external asymmetric Ni–O stretching modes, respectively [120]. The peak at 581 cm$^{-1}$ is assigned to Ni–O symmetric stretching vibration mode [119,121,122]. It is interesting to observe that the absorption peak at 581 cm$^{-1}$ is slightly higher (Fig. 8(b)–(d)) than that of pure NiO peak in (Fig. 8(e)). This increase could be due to the higher adsorption of vibrational energy by the NiO species after the impregnation of HMS [118,121]. Therefore, this result can be attributed to the formation of Si–O–Ni bonds, which is also comply with the FT-IR results (Fig. 7). In fact, Ni–O has low oxidation states (Ni$^{2+}$) which may indicate that Ni can be accommodated in the lattice of SiO$_4$ [121]. This phenomenon is in good agreement with previous Raman studies [118,119,122].

3.1.7. Temperature programmed desorption-ammonia (TPD-NH$_3$) analysis

The quantitative analysis of the temperature programmed desorption of ammonia (TPD-NH$_3$) is carried out to identify the total acidity and acid strength of different Ni loading supported on mesoporous HMS as shown in Fig. 9. The pure NiO (100 wt% Ni) is analyzed to compare it with the series of Ni/HMS catalysts. Typically, the TPD-NH$_3$ curve could be deconvoluted into three types of NH$_3$ desorption peaks; where the temperature of 100–250 °C, 250–400 °C and $\geq$400 °C correspond with the weak acid, moderate acid, and high acid strength respectively [123,124]. The total amount of NH$_3$ for all NiO and HMS catalysts is summarized in Table 2. As we can see, the maximum of NH$_3$ desorption rate from the highest and lowest are shown in the following order; 10 wt% Ni/HMS > 40 wt% Ni/HMS > 5 wt% Ni/HMS > 100 wt% Ni > HMS. The pure HMS catalyst exhibits a major peak around $\sim$471 µmol of NH$_3$·g$^{-1}$, corresponding to the weak acid sites at a temperature of 110 °C due to the silanol (Si–OH) and siloxane (Si–O–Si) groups. This can be ascribed to the desorption of weakly
bound ammonia on the surface of the HMS catalyst [125]. Meanwhile, the pure NiO has two smaller peaks, appearing at 425 °C and 590 °C respectively which generate a strong acidity with 545 µmol of NH₃g⁻¹ in the TPD-NH₃ profile (Fig. 9). However, the incorporation of Ni into HMS has generated new acid sites of weak and moderate strengths. As evidence, the total acidity level increases up to 1537 µmol of NH₃g⁻¹ for the 10 wt% Ni/HMS catalyst. It is observed that the 10 wt% Ni/HMS exhibit a weak and strong level of acidity at 150–170 °C and 490–700 °C respectively. This is because the high surface area, coupled with the interaction of HMS and NiO has enhanced the formation of additional acid sites. This finding aligns with the previous study in which Ni interacted with Si-OH to form a new acid site exhibited by the Si-O-Ni bonding compared to the pure nickel oxide (NiO) [93,110,126]. Thus, this result is in good agreement with FT-IR (Fig. 7) and RAMAN (Fig. 8).

3.2. Deoxygenation of triolein activity

Fig. 10 shows the triolein conversion from DO reaction and the conversion decreased in the following order: 10 wt% Ni/HMS (92.5%) > 40 wt% Ni/HMS (88.6%) > 5 wt% Ni/HMS (87.7%) > 100 wt% Ni (79.1%) > HMS (75.2%) catalysts. Among these catalysts, 10 wt% Ni/HMS exhibit the highest conversion which is 92.5%, more than that of HMS (75.2%). This significant enhancement is due to the higher and stronger acidity. Notably, hydrocarbon from C₈ to C₂₀ represents the major products (Fig. 11). Interestingly, 10 wt% Ni/HMS catalyst shows a higher degree of selectivity of 95.2% for the diesel range (C₁₁–C₂₀) (Fig. 12b). This phenomenon is in accordance with the reduction of carboxylic acid upon incorporation of Ni on HMS support. It has also been reported that the addition of Ni increases the decarboxylation/decarbonylation [127,128]. Furthermore, 10 wt% Ni/HMS displays a higher degree of selectivity for C₁₅–C₁₇ (∼76.79%) (Fig. 12(a)). This result illustrates that the hydrocarbon distribution is selectively composed of C₁₅–C₁₇ via decarboxylation pathway. The secondary cracking of C₁₅–C₁₇ leads to the formation of C₁₁–C₁₄ (12.31%) over 10 wt% Ni/HMS (Fig. 11) which can be due to mild cracking. The superior performance of the 10 wt% Ni/HMS is attributed to the higher acidity (µmol of NH₃g⁻¹: ∼1537) (Fig. 7) and the presence of large surface areas (S_BET: ∼512 m²/g). The presence of this higher amount of acidity could be due to the interaction between HMS and Ni that leads to the formation of the Si–OeNi species in the catalyst structure. This clearly implies that the 10 wt% Ni/HMS catalyst has induced the C–C cleavage and C–O cleavage via cracking and decarboxylation/decarbonylation reactions respectively. This finding is consistent with the product distribution and demonstrates the importance of Ni in facilitating the DO reaction. As the Ni loading increases up to 40 wt%, the conversion and diesel selectivity (C₁₁–C₂₀) decrease to 88.6% and 94.5% respectively. This detrimental effect is consistent with the TPD-NH₃ result (Fig. 9), in which 40 wt% Ni/HMS exhibit lower acidity of ∼1157 µmol of NH₃g⁻¹ compared to that of 10 wt% Ni/HMS catalyst.

Fig. 10. Triolein conversion (wt%). Reaction conditions; triolein: 10.0 g; catalyst: 0.5 g; T = 380 °C; t = 2 h. Error bars reflect the average of three independent catalytic tests.

Fig. 11. Product distribution of the hydrocarbon liquid product (%) upon deoxygenation of triolein. Reaction condition: reaction time (t): 2 h; temperature (T): 380 °C. Error bars reflect the average of three independent catalytic tests.

Fig. 12. (a) Carbon distribution of hydrocarbon liquid product (C₈–C₂₀) and (b) selectivity of diesel (C₁₁–C₂₀). Reaction conditions; triolein: 10.0 g; catalyst: 0.5 g; T = 380 °C; t = 2 h. Error bars reflect the average of three independent catalytic tests.

HMS catalyst shows a higher degree of selectivity for 95.2% for the diesel range (C₁₁–C₂₀) (Fig. 12b). This phenomenon is in accordance with the reduction of carboxylic acid upon incorporation of Ni on HMS support. It has also been reported that the addition of Ni increases the decarboxylation/decarbonylation [127,128]. Furthermore, 10 wt% Ni/HMS displays a higher degree of selectivity for C₁₅–C₁₇ (∼76.79%) (Fig. 12(a)). This result illustrates that the hydrocarbon distribution is selectively composed of C₁₅–C₁₇ via decarboxylation pathway. The secondary cracking of C₁₅–C₁₇ leads to the formation of C₁₁–C₁₄ (12.31%) over 10 wt% Ni/HMS (Fig. 11) which can be due to mild cracking. The superior performance of the 10 wt% Ni/HMS is attributed to the higher acidity (µmol of NH₃g⁻¹: ∼1537) (Fig. 7) and the presence of large surface areas (S_BET: ∼512 m²/g). The presence of this higher amount of acidity could be due to the interaction between HMS and Ni that leads to the formation of the Si–O–Ni species in the catalyst structure. This clearly implies that the 10 wt% Ni/HMS catalyst has induced the C–C cleavage and C–O cleavage via cracking and decarboxylation/decarbonylation reactions respectively. This finding is consistent with the product distribution and demonstrates the importance of Ni in facilitating the DO reaction. As the Ni loading increases up to 40 wt%, the conversion and diesel selectivity (C₁₁–C₂₀) decrease to 88.6% and 94.5% respectively. This detrimental effect is consistent with the TPD-NH₃ result (Fig. 9), in which 40 wt% Ni/HMS exhibit lower acidity of ∼1157 µmol of NH₃g⁻¹ compared to that of 10 wt% Ni/HMS catalyst.
It is noteworthy to observe that HMS support is also capable of producing 79.5% selectivity for diesel (Fig. 12(b)). This is caused by the existence of weak acid sites (471 µmol of NH₃/g) and siloxane (Si–O–Si) linkages, which is the main characteristic of HMS support [107,129]. It is reported that the HMS comprises both Lewis and Bronsted acid sites [130]. The Si–OH group leads to the formation of weak Bronsted acid sites [93,118,131]. Meanwhile, the generation of Lewis acid sites is attributed to the Si–O–Si bonds [132,133]. However, the influence of silanol (Si–OH) groups in HMS has rendered a synergistic effect of the cracking and decarbonylation of triolein. As a result, the triolein experiences direct decarbonylation, decarbonylation, and cracking. Subsequently, a few saturated acids undergo decarboxylation reactions, which transform them into shorter hydrocarbons (C₈-C₁₂) as previously suggested by Yakovlev et al., 2009 [137], leading to the formation of saturated acids (e.g., octanoic acid, nonanoic acid, decanoic acid, and undecanoic acid). The formation of saturated acid over HMS support indicates that the HMS had a mild cracking influence of the cracking and decarboxylation of oleic acid. Na et al. also reported a similar finding, 2010 [134], in which the weak acid sites produced greater amounts of fatty acids. Therefore, it can be deduced that the synergistic effect between HMS and Ni significantly increases the strength of the acid and subsequently enhances the DO reaction via decarbonylation, decarbonylation and cracking.

3.3 Reaction pathway for the deoxygenation of triolein over Ni/HMS catalysts

By considering to the product distribution from GCMS results, a variety of intermediate products during the deoxygenation of triolein is shown, as presented in Fig. 11. An important note is that the hydrocarbon with odd n-carbon atoms (C₉, C₁₁, C₁₃, C₁₅, C₁₇, and C₁₉) is found to be slightly higher than those with even n-carbon atoms (C₈, C₁₀, C₁₂, C₁₆, C₁₈, and C₂₀). Indeed, the hydrocarbon with even n-carbon atoms is more symmetrical than those with odd n-carbon atoms of hydrocarbon [135,136]. Furthermore, the hydrocarbon with odd n-carbon atom has a higher melting point, and thus greater energy is required to break the hydrocarbon chain with the even n-carbon atoms. Therefore, the main reaction pathway of the deoxygenation (DO) is through decarbonylation, decarbonylation, and cracking, as presented in Fig. 12 [62]. First, the triolein underwent C–C bond scission via the β-elimination of hydrogen to form 1 unit of oleic acid (C₁₈H₃₄O₂). The resulting oleic acid can be further cracked by removing of the terminal carbons (CH₂–) as previously suggested by Yakovlev et al., 2009 [137], which then hydrogenates 8-heptadecene as by-products.

The latter 2 units of oleic acids (C₁₈H₃₄O₂) underwent cracking via H-transfer which is accompanied by β-elimination (cleavage of a σ-bond and formation of π-bond), then followed by the decarbonylation, simultaneously releasing CO₂ and ethylene (CH₂=CH₂) as by-products. The subsequent oleic acid was decarboxylated (−CO₂) to give 8-heptadecene (C₁₇H₃₄) as the primary product. In this study, the higher amount of C₁₅-C₁₇ was observed upon contact with Ni. Therefore, it can be deduced that the resulting heptadecane undergoes the reaction through hydrogenation. The presence of the acid catalyst from Ni/HMS catalyst facilitates the transfer of H⁺ which then hydrogenates 8-heptadecene (C₁₇H₃₄) to produce the corresponding heptadecane (C₁₇H₃₆) [138]. Alternatively, the oleic acid can be converted into 8-heptadecene (C₁₇H₃₄) through decarbonylation, simultaneously forming carbon monoxide (−CO) and water (H₂O). As a result, the in-situ-produced H₂
sources via water gas shift reaction (WGS) (CO + H₂O → CO₂ + H₂) can be used to transform heptadecane (C₁₇H₃₆). This phenomenon is in accordance with a previous study, which shows that the WGS reaction occurs naturally during decarbonylation, thereby releasing CO₂ and H₂ [139]. In addition, it has been proved that the DO reaction in this study has a small amount of cyclic compound which is composed of approximately at ≤5% (Fig. 11). In this case, the cyclic compound has been proposed via cyclization of the unsaturated compound to n- cycloalkanes [140]. Similarly, these results are in agreement with previous studies [141–144].

4. Conclusion

In this study, the Ni/HMS catalysts have shown a significant effect in the deoxygenation of triolein to produce biofuel-like hydrocarbon. The selectivity of the Ni/HMS catalyst has improved tremendously; up to 95% of the diesel range (C₁₁–C₂₀). This improvement is mainly due to the synergistic effect of Si−O−Ni bonds, which lead to the formation of strong acid sites in the Ni/HMS catalysts. Therefore, the introduction of Ni ions on the mesoporous HMS by incipient wetness impregnation has positively enhanced the DO reaction.

Acknowledgments

The authors are very grateful for the financial support of the Fundamental Research Grant (F054-2013B), University of Malaya Research Grant (UMRG) RP025A/B-C1/14AET, SATU grant (RU018D-2016), Postgraduate Research Fund Scheme (PG051-2015A) and my SBUM scholarship from University of Malaya (UM). Gratitude is also extended to the infra lab team; especially to Mrs. Farah Diana Idris, Mr. Jebri Sulaiman, Mr. Jasmi Abd. Aziz (IPPP, UM) and Mr. Zailan Mohd Yusof (Department of Physic, FST, UKM) for their kind assistance in GC/MS, BET and low angle XRD analysis.

References

S. Zulkepli et al.

Energy Conversion and Management 2018 (495) 498–508


