Surface-silanised and alkoxylated micro-mesoporous Ni/hierarchical nanozeolites for oleic

acid hydrodeoxygenation

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Abstract

In this work, we report a novel and green method for the synthesis of hierarchical nanozeolites for the hydrodeoxygenation of oleic acid to diesel-range hydrocarbons. Hierarchical nanozeolites based on HZSM-5 and HBEA with appropriate mesopores (8-20 nm) were synthesised through the surface silanisation of zeolitic seeds. In this method, organosilane (hexadecyltrimethoxysilane) was used as a growth inhibitor while biomass-derived alcohols (1-decanol and iso-butanol) were used to improve the miscibility and dispersion of the organosilane. ¹H MAS NMR analysis confirmed the silanisation and alkoxylation of the zeolitic seeds. The physicochemical properties of the catalysts were analysed by XRD, N₂ porosimetry, NH₃-TPD, pyridine-DRIFTS, XPS and TEM, and the catalytic performance of bifunctional 10 wt.% Ni/h-HZSM-5 and Ni/h-HBEA were then evaluated in the HDO of a bulky feedstock, oleic acid. The hierarchical zeolites supported Ni catalysts achieved more than 86% conversion of oleic acid. Compared with their microporous nanozeolite counterparts, Ni/h-HBEA and Ni/h-HZSM-5 exhibited comparable or higher Brønsted/Lewis acid ratios, leading to high selectivity towards C18 alkanes (65% and 71%, respectively); they also demonstrated similar catalytic yields. More importantly, while their microporous analogues lost much of their activity after the first cycle, Ni/h-HZSM-5, in particular, displayed excellent stability, even after four cycles. Thus, our approach appears to be a promising way of preparing catalyst supports for efficient hydrotreatment of bulky substrates.

Keywords: Hierarchical, Nanozeolite, Hydrodeoxygenation, Green diesel

1. Introduction

With multiple energy crises and environmental difficulties associated with both petrodiesel and FAME-based biofuels, the production of green diesel via the hydroconversion (HC) of wastederived free fatty acids and lipids offers a promising route to alternative fuels [1-3]. As shown in **Scheme 1**, depending on the catalyst and reaction conditions used, the HC of fatty acids can occur via three main pathways: hydrodeoxygenation (HDO), hydrodecarbonylation (HDC) or decarboxylation (DCO) [4-6]. HDC or DCO yield hydrocarbons with one carbon atom less than the original reactants and CO or CO_2 as by-products. HDO, on the other hand, is a particularly interesting HC process as it results in the production of *n*-alkanes with the same carbon chain length as the starting feedstock and water. The calculation for the enthalpy of reactions of oleic acid HC is shown in **Scheme S1**.



Scheme 1. Deoxygenation pathways of fatty acid molecules during HC process

Bifunctional transition-metal solid-acid catalysts promote fatty acid and lipid HDO by hydrogenating C=C and C=O bonds over its metallic component and dehydrating aliphatic oxygenates by the acidic sites present in the support [6-8]. In this respect, metal-doped zeolites are promising catalysts for the HDO of various organic compounds, including free fatty acids and lipids [9-11]. However, their microporous structure exhibits poor in-pore diffusion for bulky feedstocks [12-14]. As a way of potentially addressing this issue, the synthesis and application of hierarchical zeolites have received much attention [15-17].

Bifunctional metal-doped hierarchical zeolites are a relatively new group of heterogeneous acid catalysts in which the integration of an additional macroporous or mesoporous framework can enhance catalytic performance, particularly in HDO [18-20]. An integrated mesopore has been shown to be beneficial in various respects: (i) it improves the mass transport of large molecules to the active sites, either metal nanoparticles (NPs) or acid sites, that are mainly positioned inside the zeolite micropores [19]; (ii) it accelerates the diffusion of the products, thereby hindering coke formation and delaying catalyst deactivation [18]; (iii) it enhances the dispersion of NPs along the porous architecture of hierarchical meso-microporous zeolites [21]. In particular, such dispersion has been shown to improve the selectivity of HDO products rather than the localization of NPs on the external surface of their typical microporous zeolites counterparts [21]. This was demonstrated by Ma et al. (2015), who reported that the HDO of stearic acid over the wide-pore hierarchical nanozeolite HBEA resulted in higher selectivity to n- and iso- C₁₈/C₁₇ hydrocarbons compared to microporous HBEA [22]. This was followed by the work of Hunns et al. (2016), showing that mcresol HDO performed over Pd incorporated on hierarchical ZSM-5 led to high conversion and selectivity to methylcyclohexane [18]. In addition, hierarchical zeolites doped with non-noble metals, such as Co [23] or Ni [24], have also been shown to be attractive catalysts for low-cost

HDO. Indeed, Ni-doped hierarchical ZSM-5 [25], HBEA [26] and USY [27] all exhibited superior activity to their respective microporous counterparts, especially in active site accessibility and activity.

In the last decade, various approaches have been used to synthesize hierarchical zeolites, including post-synthesis (dealumination/desilication of microporous zeolites) and direct-synthesis (hard or soft templating) methods [28, 29]. The post-synthesis method has been shown to have several disadvantages, such as destruction of the zeolite's crystalline structure, changes in its acidic properties, and random mesopore formation during the synthesis [30, 31]. Consequently, the use of a soft template, such as that provided by organosilanes, has emerged as an attractive method for the preparation of hierarchical nanozeolites. In surface passivation soft templating, the bulky organosilane groups become attached to the exterior region of the zeolitic seeds, thereby preventing the growth of the zeolite crystals and their formation into larger structures. Simultaneously, the spaces initially occupied by the organosilanes generate mesopores upon thermal decomposition. This strategy has been employed in the synthesis of many hierarchical nanozeolites (ZSM-5, zeolite Beta, mordenite, etc.) not only improve their textural features but also greatly enhance their catalytic properties [32-36]. Typically, the obtained hierarchical nanozeolites are 200-400 nm aggregates consisting of tiny nano units below 10 nm [37].

Compared to the solventless synthesis described above, the synthesis of hierarchical nanozeolites using a soft template in the presence of an organic solvent leads to more stable zeolites with a narrower distribution of zeolite nanoparticles [37-40]. The organic solvent can disperse the grafted nanocrystals and prevent them from substantial agglomeration, resulting in fine particles. The use of short-chain alcohols increases the efficiency of organosilane grafting and of alkoxylation on the zeolite surface, leading to further enhancement of the textural properties and

quality of the final materials [38]. The employment of straight-chain alcohols, such as ethanol and *n*-butanol, stabilises the zeolite nanoparticles during silanisation, ensuring higher quality zeolites, but large aggregates (200-400 nm) are ultimately still formed. Utilising two-phase (toluene/1-butanol mixtures) [39] or single-phase (formamide or toluene) [40] systems can reduce such aggregation, producing small 20-50 nm nanozeolites. In particular, the toluene/1-butanol mixture appears to be a good choice for synthesizing nanosized hierarchical zeolites as it increases the miscibility of organosilane, leading to effective silanisation and alkoxylation [39]. However, the hazards and environmental problems associated with the use of organic solvents, such as formamide [41] and toluene [42, 43], in the synthesis of hierarchical zeolites limits their application on an industrial scale.

Here, to the best of our knowledge, we are the first to report the green-solvent-assisted synthesis of surface-silanised and alkoxylated hierarchical nanozeolites Beta and ZSM-5 doped with relatively inexpensive Ni NPs. Accordingly, potentially renewable and less harmful alcohols are used as solvents for sustainable zeolite silanisation and alkoxylation. Based on preliminary screening conducted in our laboratory, bio-derived 1-decanol and *iso*-butanol are used for the ZSM-5 and Beta syntheses. Using the HDO of oleic acid (one of the main components of many waste-oil feedstocks) as a model reaction, the efficiencies of Ni supported on hierarchical nanozeolite catalysts are compared with those of microporous nanozeolites and commercial zeolites. More significantly, with a reusability study, the hierarchical nanozeolites proved better in-pore diffusion for bulky molecules and delayed deactivation.

2. Experimental

2.1 Chemical and Materials

All purchased materials were used directly without any additional refinement. The Ni catalyst was prepared using nickel(II) nitrate hexahydrate (Ni(NO₃)₂.6H₂O) salt, which was obtained Sigma-Aldrich, USA. tetraethylorthosilicate (TEOS, from The 98%); tetraethylammonium hydroxide (TEAOH, 35 wt.%), tetrapropylammonium hydroxide (TPAOH, 20wt.%), hexadecyltrimethoxysilane (HDTM) (≥ 85%), oleic acid (90 wt.%), aluminium sulphate hexadecahydrate (Al₂(SO₄)₃.16H₂O \geq 95%), 1-bromohexane (98%), potassium bromide (KBr, 99%) and pyridine (99%) were also obtained from Sigma-Aldrich, USA. Sodium aluminate (NaAlO₂) and fumed silica (SiO₂) were purchased from Sigma-Aldrich, Germany. Meanwhile, sodium hydroxide (NaOH, 99%) was procured from R&M Chemicals, U.K. 1-Decanol and isobutanol were bought from Merck Chemicals, USA. The commercial zeolites ZSM-5 ammonium (Si/Al = 15) and Beta ammonium (Si/Al = 19) were procured from Alfa Aesar, USA. Hydrogen (purity 99.9%) and nitrogen (purity 99.9%) were obtained from Polygas Sdn. Bhd. (Malaysia), and 5 vol.% of H₂ in argon was bought from Linde Malaysia Sdn. Bhd. company. Alkane standard solution (C₈-C₂₀) containing 40 ppm concentration of each hydrocarbon in hexane was purchased from Sigma Aldrich, USA.

2.2 Preparation of Hydroconversion Catalysts

2.2.1 Preparation of Zeolite Support

Zeolite Beta and ZSM-5 were synthesised according to the methods modified from the literature [39, 44]. The microporous nanozeolite Beta was prepared from an initial aluminosilicate gel with a molar ratio of 60 SiO₂: 1 Al₂O₃: 3 Na₂O: 32 TEAOH: 421 H₂O. Typically, 0.11 g of NaAlO₂ and 0.07 g of NaOH were dissolved in a 250 mL teflon beaker containing 3.21 g of H₂O. Then, 14.65 g TEAOH was added dropwise to the above solution. After stirring for 15 min, 1.96 g of fumed silica were dissolved in the gel solution. The ZSM-5 samples were prepared from an aqueous clear gel solution with a molar ratio of 60 SiO₂: 1 Al₂O₃: 32 TPAOH. Initially, 3.35 g of TEOS was added into the 6.50 g TPAOH solution and stirred for 15 min with the subsequent addition of 0.22 g of Al₂(SO₄)₃.16H₂O. The resulting Beta and ZSM-5 gels were then aged for 24 h at room temperature.

The hierarchical nanozeolites were synthesised from the same gel compositions as the microporous zeolites. The zeolite precursor gels were grafted with HDTM after the ageing process, according to a method reported in the literature with some modifications [39, 45]. The grafting of hierarchical nanozeolites Beta (h-HBEA) and ZSM-5 (h-HZSM-5) with HDTM was carried out using potentially renewable iso-butanol and 1-decanol, respectively. The corresponding zeolite gel was added in 40 mL of the organic solvent containing HDTM. The amounts of HDTM used were 10 mol % and ~ 19 mol % with reference to the total amount of silica in the starting gel solution of Beta and ZSM-5, respectively. The mixture was kept under reflux at 80 °C and stirred for 12 h.

The pre-crystallised gels obtained in the above-mentioned syntheses (with and without HDTM) were crystallised at 150 °C using a teflon-lined stainless-steel autoclave under autogenous

pressure for 5 days. The resulting crystalline products were recovered by centrifugation, washed several times with deionised water and then oven-dried at 110 °C. The final products were calcined at 550 °C for 5 h with 1 °C min⁻¹ ramp rate. The acidic type of zeolites was prepared by ion-exchange treatment with 1.0 M ammonium nitrate solution. The zeolite samples were stirred for 4 h at 80 °C, then washed with deionised water and thoroughly dried in the oven. The dried products were subsequently activated at 550 °C for 4 h with 3 °C min⁻¹ ramp rate. As a result, the protonic forms of HZSM-5 and HBEA were obtained.

The microporous nanozeolites ZSM-5 and Beta synthesised without the HDTM organosilane surface functionalisation were designated as m-HZSM-5 and m-HBEA. On the other hand, the hierarchical nanozeolites synthesised with the HDTM-functionalisation step were denoted as h-HZSM-5 and h-HBEA. As a comparison, the catalytic performances of commercial microporous zeolites regarded as c-HZSM-5 and c-HBEA (Alfa Aesar) were also investigated along with other supports in this study.

2.2.2 Synthesis of Ni-Supported Catalysts

The incorporation of 10 wt. % Ni on the acidic supports was conducted via the wet impregnation method described previously [46]. Briefly, the required amount of Ni(NO₃)₂.6H₂O was dissolved in deionised water and added dropwise to the support material. The amount of water used in this synthesis was fixed based on the total weight of the catalyst prepared. For every 2 g of catalyst prepared, 10 mL of water was used to dissolve the metal salt and impregnate the zeolite materials. The wet catalyst was stirred under ambient conditions for 4 h. Subsequently, it was heated to 80 °C until the water was completely evaporated. The catalyst was further dried overnight

in an oven at 110°C and lastly calcined at 500 °C for 2 h in air with a 3 °C min⁻¹ ramp. All the catalysts were reduced to metallic form before characterisations and catalytic tests at 580 °C for 5 h under the flow of 5% vol. H₂ in Ar with 2 °C min⁻¹ heating rate.

2.3 Characterisation of Catalysts

All the catalysts were characterised after calcination unless otherwise specified. All activated Ni-supported catalysts were extensively characterised. The phase identification and crystallinity of the catalysts were analysed by wide-angle powder XRD using a Shimadzu XRD-6000 diffractometer (Japan), with Cu K_a radiation with a wavelength of $\lambda = 0.154$ nm. The scanning was in the 20 range between 5° and 90° with a scan rate of 2° min⁻¹.

The morphological analyses of the synthesised catalysts were carried out at 20 kV using a FESEM JEOL (JSM-7600F, Japan). The samples were spread on a carbon tape and coated with platinum prior to the analysis.

Hydrogen temperature-programmed reduction (H₂-TPR) and ammonia temperatureprogrammed desorption (NH₃-TPD) analyses were performed on a Thermo Finnigan TPDRO analyser (model 1100 series, USA) with a thermal conductivity detector (TCD). About 50 mg of the sample was pre-treated at 150 °C with a heating ramp of 10 °C min⁻¹ for 1 h. The sample was then cooled down to 50 °C before the analysis proceeds using a reducing agent comprised of a gas mixture containing 5% vol. H₂ and 95% vol. Ar with a total flow rate of 30 mL min⁻¹. The TPR profile was recorded up to 950 °C with a 10 °C min⁻¹ ramp rate and held at that temperature for 30 min. To measure the acid site concentrations by NH₃-TPD, the pre-treated samples were saturated with NH₃ for 1 h at ambient temperature. The excess NH₃ was flushed out using pure N₂ at room temperature for 35 min. The NH₃-TPD profile was recorded from 50 °C to 950 °C at a heating rate of 10 °C min⁻¹ under 30 mL min⁻¹ flow of He and held for 30 min.

The specific surface area was measured using an N₂ adsorption/desorption method on a Thermo Fisher Scientific instrument (model SURFER) at -196 °C. The sample was degassed at 200 °C for 12 h under vacuum condition of 10^{-2} torr and 1 h at 10^{-6} torr prior to the analysis. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) equation. Pore size distributions of the catalysts were determined using the Barrett-Joyner-Halenda (BJH) method applied to the desorption branch of the isotherms.

The thermogravimetric (TGA) analysis of the spent catalysts was performed on TGA Mettler Toledo 990, where the catalyst was heated from 50 to 900 °C with a heating rate of 10 °C min⁻¹ and an O_2 flow of 40 mL min⁻¹.

The particle size distributions of catalysts were measured using a high-resolution transmission electron microscope (HRTEM) on a JEOL 2100-F microscope (Japan) at 200 kV. Samples were prepared by dispersing in methanol, followed by drop casting onto Cu holey carbon grids (100 mesh) and evaporating at ambient temperature.

The Brønsted and Lewis acid character of the catalysts were analysed by pyridine-adsorbed diffuse reflectance infrared Fourier transform spectroscopy (pyridine-DRIFTS) analysis using a Thermo Scientific Nicolet iS50 FTIR spectrometer (USA) at ambient temperature. The sample was ground with 50 wt.% KBr solid into a fine powder, wetted with 0.1 mL of pyridine. Prior to the analysis, the sample was dried in the fume hood for 1 h, then dried overnight in the vacuum oven at 40 °C. The DRIFT spectra of samples were processed using OMNIC 9.2.98 software by subtracting the spectra of untreated parent samples (acted as a background). The relative Brønsted-

Lewis character was calculated from the absorbance ratio at 1545-1535 cm⁻¹ and 1445-1450 cm⁻¹.

Bulk elemental compositions of the catalysts were determined using inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Thermo Scientific iCAP 7000 series, USA).

The information about the surface chemical environment and elemental composition of the catalysts was acquired by X-ray photon spectroscopy (XPS) using an Axis HSi (Kratos, UK) spectrometer fitted with an Al K α (1486.6 eV) monochromated radiation source and a charge neutraliser with a pass energy of 40 eV. All the spectra were calibrated with reference to adventitious carbon peak at 284.6 eV. Peak fitting was performed with CASA XPS v2.3.18 PR1.0 software. The catalyst was reduced as specified in section 2.2.2 and stored under vacuum until use in the XPS analysis. The reduced catalyst was also somewhat exposed to air during the sample preparation stage.

The grafting of the HDTM and alkoxyl species in the as-made hierarchical ZSM-5 was investigated with Proton magic angular spinning nuclear magnetic resonance (¹H MAS NMR). The ¹H MAS NMR experiment was conducted using a high-resolution Bruker AVANCE III HD 400 spectrometer (USA) at a magnetic field strength of 11.7 T. ¹H MAS NMR spectrum was recorded with reference to tetramethylsilane using a 2.6 μ s $\pi/2$ pulse, a recycle delay of 2 s and 256 transients.

2.4 Catalytic Test

The catalytic HC of commercial-grade oleic acid was performed in a custom-built stainless-steel batch reactor (30 mL volume) equipped with an overhead stirrer attached to a long

impeller, as shown in Fig. S1. The sample mixture containing 5 g of feedstock (oleic acid) and 0.25 g of catalyst without any solvent was added to the reactor. A solvent-free HDO reaction would be ideal for industrial applications [47]. Initially, the reactor was purged with N₂ for 20 min at 40 °C to remove the oxygen molecules dissolved in the sample. Subsequently, the reactor was purged with high-purity H₂ gas for 15 min to remove the remaining N₂. The HC reaction was conducted by pressurising the reactor with 50 bar H₂ gas and heating it to the specified temperature (350-400 °C) with a ramp rate of 10 °C min⁻¹ and a stirring speed of 200 rpm started after reaching the desired temperature. Once the reactor reached the desired temperature, the pressure ultimately rose to 80 bar. After 2 h, the reactor was cooled down to room temperature, and the effluents, containing both liquid and gas, were withdrawn separately for gas chromatography (GC) analysis. The liquid product was weighed before being analysed by gas chromatography. The gaseous sample was collected using a 100 mL gas sampling bag with a polypropylene valve. For the catalyst recyclability test, the solid catalyst was regenerated by filtrating from the liquid product, followed by rinsing with hexane and drying in the oven at 100 °C before reuse in the next reaction cycle.

2.5 Product Analysis

2.5.1 Liquid Product Analysis

The conversion, yield and selectivity of the liquid products were determined using gas chromatography equipped with a flame ionisation detector (GC-FID) from Agilent Technologies (6890 model, USA) and a non-polar capillary column (HP-5, length: 30 m × inner diameter: 0.32 mm × film thickness: 0.25 μ m). 2 μ L of liquid product was dissolved in 1.5 mL of GC grade *n*hexane prior to the analysis. The hydrocarbons were quantified based on the standard alkane solution (C₈-C₂₀) relative to an internal standard (1-bromohexane). 1.0 μ L of the sample was injected into the GC operated in split mode (split ratio = 5) and at an inlet temperature of 250 °C. The flow rate of the carrier gas (He) was 1 mL min⁻¹. The oven temperature was initially started at 40 °C and held for 2 min, then raised to 260 °C at a heating rate of 12 °C min⁻¹ and then held for 10 min.

The conversion of oleic acid was calculated from Equation 1, where n_0 is the initial moles of oleic acid prior to the addition of hydrogen, and n_t is the moles of unconverted oleic acid after the reaction. The percentage yield was determined from Equation 2 based on the C₈-C₁₈ alkane products formed. Selectivity of C₁₇ and C₁₈ hydrocarbons was defined using Equation 3, the sum of moles of C₁₇ or C₁₈ alkanes (including normal and iso alkanes) divided by the total amount of hydrocarbon products detected. The HDO / HDC or DCO selectivity was discussed based on the ratio of *n*-C₁₈ to *n*-C₁₇ according to Equation 4. The carbon balance was calculated based on Equation 5.

$$\% conversion = \frac{(n_o - n_t)}{n_o} \times 100\%$$
⁽¹⁾

% yield of hydrocarbon

$$= \frac{Total \ mmol \ of \ alkane \ in \ the \ range \ of \ C_8 - C_{18} \ in \ the \ liquid \ product}{Initial \ mmol \ of \ oleic \ acid} \times 100 \ \%$$
(2)

% selectivity of C_{17} or C_{18}

$$=\frac{Yield \ of (n + iso \ C_{18}) \ or \ (n + iso \ C_{17}) hydrocarbons}{Total \ yield \ of \ hydrocarbons \ in \ the \ product} \times 100 \ \%$$
(3)

Ratio of
$$\frac{nC_{18}}{nC_{17}} = \frac{\text{yield of } nC_{18} \text{ alkanes}}{\text{yield of } nC_{17} \text{ alkanes}}$$
 (4)

Carbon balance

 $=\frac{moles of \ carbon \ in \ [gaseous \ (CO_2 + CO + CH_4) + liquid \ (C_8 - C_{18}) \ products + unconverted \ oleic \ acid]}{Initial \ moles \ of \ carbon \ in \ oleic \ acid}$

imes 100 %

(5)

2.5.2 Gas Product Analysis

For the gas analysis, 0.25 mL of sample was withdrawn directly from the sampling gas bag using a PTFE Luer lock gas-tight syringe. Then, the aliquot was manually injected through an offline GC (Agilent Model G1540N, USA) connected to a thermal conductivity detector (TCD). The gaseous products were separated by two types of columns (HP-PLO/Q and HP-MOLSIV) using high purity He (99.999%) as a carrier gas with a flow rate of 20 mL min⁻¹. The inlet and oven temperatures were maintained at an isothermal mode of 60 °C throughout the analysis. The detector temperature and data rate were set at 150 °C and 20 Hz. The volume composition of the gas products such as CO, CO₂, CH₄ and H₂were calculated was calculated using calibrations based on standard gas mixtures. The standard gas mixture contains H₂ (100300 ppm or 10 mol %), CO (1018 ppm, 0.1 mol %), CO₂ (1017 ppm, 0.1 mol %), CH₄ (1017 ppm, 0.1 mol %) and the remaining volume was balanced with He. The Agilent HP-PLOT/Q column (30.0 m x 0.53 mm x 40.0 µm) was packed with polystyrenedivinylbenzene material that facilitated the elution of CO₂, whereas H₂, CO and CH₄ gases were separated using an Agilent HP-MOLSIV column (30 m x 0.53 mm x 50 µm).

2.5.3 Qualitative Analysis

The product distribution and by-product formation in HC reaction were determined using gas chromatography-mass spectroscopy (GC-MS, Shimadzu QP2010) equipped with an RTX-5 MS column (30 m x 0.25 mm x 0.25 μ m). 1 μ L of aliquots was injected in splitless mode with the inlet temperature set at 250 °C with a constant flow of He gas at a flow rate of 1 mL min⁻¹. The GC oven temperature was initially maintained at 40 °C for 3 min, then increased to 250 °C at 7 °C min⁻¹ and held continuously for 5 min. The temperature was then ramped up to 300 °C at 15 °C min⁻¹ and finally held for 5 min. The MS detector was operated at an ion source and interface temperature of 240 °C and 300 °C, respectively. The qualitative profile was obtained by scanning the mass spectrum in the m/z SCAN range of 35 to 450 amu.

3. **Results and Discussion**

3.1 Catalysts Characterization

The incorporation of alkoxyl and silanol groups on as-made hierarchical materials was confirmed by ¹H MAS NMR (**Fig. S2**). The spectrum shows features characteristic of zeolite templates TPA⁺ (1.2-1.4, 5.5 and 11 ppm) and TEA⁺ (1.0 and 3.2 ppm), mid-chain alkyl group in the HDTM (1.7-1.8 ppm) and O-CH₂ of n-decanoxy (3.5 ppm) and n-isobutoxy (3.4 ppm) bound to surface silanols [38]. Elemental analysis in **Table S1** shows that all the hierarchical materials have a slightly higher Si/Al ratio than the corresponding m-HZSM-5 and m-HBEA, which confirms the success of silanisation with HDTM [32]. The bulk elemental analysis of catalysts shows that the actual Ni content of the catalysts is very close to the nominal 10 wt.% (**Table 1**). The chemical environment and oxidation state of Ni were also probed by XPS. As presented in **Fig. S3**, the spectra of Ni 2p_{3/2} have complex shapes, composed of various oxidation states and satellite features. The peaks at 852.9 eV are attributable to the presence of metallic Ni, and broad features centred at 856.1 eV can be ascribed to Ni in oxidised (NiO) and hydroxide (Ni(OH)₂) forms. Strong satellite peaks are also observed at 861.5 eV attributed to oxo-Ni species [48-50]. The comparison of the Ni $2p_{3/2}$ region of XP spectra for the different synthesised and commercial zeolites suggests that the binding energy of Ni species does not depend on the zeolite type or its pore architecture. Thus, any difference in the performance of catalysts can be attributed to the other physicochemical properties of the catalysts, particularly to the support textural and acidic character.

 Table 1. Physicochemical properties of Ni-doped microporous and meso-microporous

 hierarchical zeolites

	Si/Al Molar ratio ^a	Ni loading a (wt.%)	Ni crystalli te size ^b (nm)	Ni disper sion ^c (%)	Acid site loading d (µmol g $^{\text{-1}}$)											
Catalyst					Temperature range (°C)			_ Total	Brønsted Acid ^e	Lewis Acid ^f	S_{BET}^{g} (m ² g ⁻¹)	S_{MIC}^{h} (m ² g ⁻¹)	S_{EXT}^{i} (m ² g ⁻¹)	V _p ^j (cm ³ g ⁻¹)	V_{MIC}^{k} (cm ³ g ⁻¹)	V_{MES}^{1} (cm ³ g ⁻¹)
					80-200	200-400	400-950				0 /	U ,	0,	0,	0,	0)
Ni/m-HZSM-5	17	8.3	20.0	5.3	776	719	90	1585	0.48	1.23	522	321	201	0.55	0.13	0.42
Ni/h-HZSM-5	18	8.5	20.7	5.2	567	507	18	1095	0.78	1.63	595	332	263	0.70	0.15	0.55
Ni/c- HZSM-5	17	8.5	25.1	-	1005	-	63	1068	0.72	1.81	358	238	120	0.31	0.10	0.21
Ni/m-HBEA	15	8.9	20.1	5.6	255	2542	209	3006	0.40	1.46	964	646	318	0.82	0.28	0.54
Ni/h-HBEA	18	9.9	20.4	6.1	826	1584	413	2823	0.40	1.61	700	486	214	1.08	0.20	0.88
Ni/c-HBEA	17	8.4	20.1	-	798	104	1504	2406	0.35	1.43	634	479	155	0.40	0.20	0.20

^a from ICP-OES (Error = ±10%), ^b from XRD Scherrer analysis; ^c Ni dispersion estimated using equation given by Scholten et al. [51] (Scheme S2) and average particle size determined from TEM, ^d from NH₃-TPD (Error = ±10%); ^e determined from the pyridine-DRIFTS Brønsted acidity absorbance peak area at 1535-1540 cm⁻¹; ^f determined from the pyridine-DRIFTS Lewis acidity absorbance peak area at 1445-1450 cm⁻¹; ^g total surface area calculated from BET equation using the P/P₀ < 0.05 (Error = ±10%). ^h S_{MIC} micropore surface area and ^k V_{MIC} micropore volume determined from t-plot analysis; ⁱ S_{EXT} external surface area was calculated from the difference between S_{BET}-S_{MIC}, ^jV_p total pore volume determined from isotherm at P/P₀=0.99 (Error = ±10%) and ¹V_{MES} mesopore volume was determined from the difference between V_p-V_{MIC}.

XRD patterns of the synthesized zeolites match the commercial ones and those reported in the literature (**Fig. S4**). Both hierarchical and microporous nanozeolites structures are crystalline when compared to the commercial counterparts, exhibiting diffractions at 7.6°, 13.4°, 14.4°, 21.2°,

and 22.2° typical of BEA and 7.9°, 8.8°, 23.1°, 23.9°, 24.4°, 25.9°, and 29.9° associated with MFI [44]. **Fig. 1(a)** shows the peaks centred at 44.84°, 52.20° and 76.84° corresponding to the [111], [200] and [220] planes of cubic Ni (JCPDS No. 04-0850). The metallic Ni phases are observed in all the Ni-doped materials (**Fig. 1b-g**), indicating successful impregnation and reduction of the loaded Ni species. As **Fig. 1b-g** shows, the incorporation of Ni nanoparticles has no significant impact on the broadening or the intensity of the diffractions arising from BEA and MFI structures, confirming that the crystalline structures of the hierarchical and microporous nanozeolites remain intact after metal impregnations.



Fig. 1 XRD patterns of Ni supported on microporous, meso-microporous, and commercial zeolites.

The isotherms of N_2 porosimetry are presented in Fig. S5 (a-o), and the textural properties of the catalysts, including the total surface area and total pore volume, are summarised in Table 1 and Table S1. The isotherms of hierarchical materials exhibit both types I and IV isotherms with an inflection point and a hysteresis loop starting from P/P_0 of 0.9 to 1.0, suggesting the coexistence of micropores and textural mesopores (interparticle voids between the aggregates of nanozeolites) [40]. The microporous m-HZSM-5 and m-HBEA possess relatively large surface areas of 747 and 1533 m²g⁻¹, as presented in Table S1. The incorporation of mesoporosity in m-HZSM-5 and m-HBEA materials resulted in a 6% and 50% decrease in the total surface areas, respectively. Furthermore, it can be observed that after the incorporation of Ni, the surface area of m-HZSM5 and m-HBEA diminishes by ~34%, suggesting micropore blockage by the Ni NPs. However, in the case of hierarchical catalysts, the surface area only decreases by ~11% after Ni doping. A plausible reason for this could be the greater degree of interparticle mesoporosity of the nanozeolites and lesser degree of agglomeration, which have contributed to a better distribution of the Ni particle formed within the solid samples, causing lesser micropore blocking [18, 52]. Additionally, Fig. S6 shows that, compared to their microporous counterparts, the hierarchical nanozeolites h-HZSM-5 and h-HBEA possess additional pores with 63 nm and 90 nm diameter, respectively, confirming the organosilane surface functionalisation facilitating higher interparticle mesoporosity. Similarly, Ni-supported on hierarchical nanozeolites (Fig. 2 iii and vi) show quite a broad pore size distribution with both small (8-20 nm) and large (20-50 nm) mesopores spanning to the external surface of zeolites compared to the corresponding commercial (Fig. 2 i and iv) and microporous nanozeolites catalysts (Fig. 2 ii and v). Moreover, due to the interparticle voids between the aggregates of nanozeolites, macropores with a broad pore size distribution (>50 nm) can be observed. In contrast, compared with the microporous nanozeolite m-HBEA support,

a slight larger pore structure spanning to the external surface area was observed in the range of 50-100 nm for the Ni/m-HBEA counterpart. This feature could be the cause of the significant obstruction of the zeolite's microporous system by the incorporated metal phase [53]. When Ni is incorporated into microporous nanozeolite m-HBEA, the total surface area S_{BET} , micropore surface area S_{MIC} , and micropore volume V_{MIC} parameters are significantly reduced to 37%, 50% and 45%, but the external surface area S_{ext} is little impacted with a small increase to 22%. This suggests that the Ni species are preferentially distributed throughout the zeolite micropores, which have a high degree of dispersion, particularly for the prepared microporous nanozeolite m-HBEA. A similar trend was observed in the previous study, indicating a decrease in zeolites' micropore surface area but an increase in their external surface area and pore diameter following the metal incorporation [53-55]. Nevertheless, it cannot be ruled out that there is a possibility some of the micropores have been blocked by the Ni particles formed.



Fig. 2 BJH pore size distributions of Ni/zeolites

TEM characterisation was carried out to examine the crystal morphology of parent zeolites (**Fig. S7**). All zeolite supports were made of aggregates of tiny primary nanocrystals with sizes around 10-15 nm. The commercial zeolites, c-HZSM-5 and c-HBEA, apparently possess larger primary particle sizes as compared with other zeolite samples. The parent hierarchical nanozeolites h-ZSM-5 and h-HBEA (**Fig. S7b** and **e**) exhibited less aggregation when compared to microporous nanozeolites m-HZSM-5 and m-HBEA (**Fig. S7a** and **d**), and commercial c-HZSM-5 and c-HBEA (**Fig. S7c** and **f**) zeolites. This is because the commercial zeolites and the microporous nanozeolites supports are solely prepared in hydrothermal condition without an organic solvent. Therefore, the primary nanoparticles tend to agglomerate intensively into larger globular aggregates during the precrystallisation and crystallisation steps (**Table S1**) [37]. Besides, the TEM images also clearly show the interparticle voids of the agglomerated nanozeolites, confirming the BJH pore sizes of more than 50 nm in **Fig. 2** and **S6** are merely the extended voids spanning to external surface of the zeolite [56, 57].

Moreover, HRTEM (**Fig. 3**) and FESEM (**Fig. S8**) characterisations were carried out to examine the morphology and distribution of the Ni supported on zeolite materials. The size of Ni particles for all catalysts was observed to be widely distributed in the range of 10-55 nm, with an average particle size of ~16-20 nm regardless of the type of support (**Fig. 3**). Metallic Ni was observed in the polycrystalline form rather than individually distributed small nanoparticles. This observation is consistent with the Ni average particle size of ~20 nm, calculated based on the XRD and Scherrer equation (**Table 1**). It is also in agreement with XPS data which shows that the surface Ni content (measured by XPS) is consistently lower than the bulk Ni content (determined by ICP-OES, **Table S2**). The depth information in XPS is defined as three times the inelastic mean free path (IMFP) of an electron through the solid [58]. As the IMFP of a Ni *2p* electron through Ni is

estimated to be 1.1 nm [59], the depth information of XPS through Ni nanoparticles will be 3.3 nm, which is significantly smaller than the average Ni particle size of the catalysts (20 nm, **Table** 1). As a large portion of the Ni content resides in the bulk of the 20 nm metal nanoparticles, due to the surface sensitivity of XPS, it is not detected. The formation of large Ni bulks can also explain the poor dispersion of Ni atoms on the support, which is less than 7% (Table 1). The main reason for the formation of large and non-uniform polycrystalline Ni species which leads to poor dispersion, is the sintering of nickel particles during the reduction stage. In this study, the impregnated nickel oxide was reduced to metallic form at a higher temperature, 580 °C for 5 h, resulting in the sintering of nickel metal particles. Besides that, the poor metal dispersion can also be attributed to the incorporation via the conventional wet impregnation technique which led to the formation of large and non-uniform particles [60]. Similar results regarding the morphology of Ni particles were observed in a previous study, where 5 wt.% Ni incorporated on HBEA via incipient wetness impregnation showed sintering of the nickel metal particles upon reduction at 560 °C. Additionally, TEM images revealed significantly larger Ni particles with average diameters of 25 nm compared to those obtained through other preparation techniques such as ionexchange, deposition-precipitation, and grafting. Moreover, the estimated dispersions of our 10 wt.% Ni on the prepared hierarchical nanozeolites are comparable to the dispersion of Ni metal supported on hierarchical HBEA reported in the literature [22]. In comparison to our study, the three times loading of Ni (about 35 wt.%) on the HBEA support leads to 3.6 % of Ni dispersion, determined from TPD-CO chemisorption.



Fig. 3 HRTEM images of (a) Ni/m-HZSM-5, (b) Ni/h-HZSM-5, (c) Ni/m-HBEA, (d) Ni/h-HBEA. Particle size distributions (inset images) are the average of 100 particles.

The reducibility of the nickel oxide phase and the impact of the porous support architecture on it were investigated by H₂-TPR analysis (**Fig. 4A**). The bulk NiO indicates reducibility below 400 °C, which is characteristic of the reduction of ionic (Ni²⁺) to metallic (Ni⁰) (**Fig. 4A a**) [61].

All the Ni-doped catalysts show the most prominent reduction peak below 400 °C, except for hierarchical nanozeolite Ni/h-HBEA (**Fig. 4A g**), which is reduced at 442 °C, characteristic of reduction temperature of a weakly bound large NiO cluster with the zeolite support [62]. The reduction peak of Ni/m-HBEA and Ni/h-HBEA exhibit a reduction shoulder at higher temperatures of 445 and 474 °C, ascribing to moderate interaction of NiO particles with the supports (**Fig. 4A f** and **g**). The reduction profiles of all the supported Ni catalysts also show a broad reduction peak centred around 520-567 °C (**Fig. 4A b-g**). The higher reduction peak is due to the reduction of Ni particles strongly bound to silica or alumina species on the zeolite surface [60].



Fig. 4 (A) H₂-TPR and (B) NH₃-TPD profiles of supported Ni catalysts

The acid sites number and strength were probed by NH₃-TPD. Fig. 4B and Fig. S9 show that the catalysts exhibit NH₃ desorption peaks in different temperature ranges. The peaks in the range of 50 to 200 °C are ascribed to the weak acidic sites, while desorption peaks in the range of 300 to 400 °C indicate moderate acidic sites. Any desorption peaks at temperatures >400 °C are associated to the strong acidic sites [63]. As presented in Table S1, the introduction of mesoporosity in the microporous zeolites led to a 34 % and 26 % decrease in the acid site loadings of HZSM-5 and HBEA, respectively. This can be explained in terms of the reduced surface area of the hierarchical zeolites. Moreover, Table 1 shows that the incorporation of Ni nanoparticles on the zeolite supports further decreases the number of acid sites, mainly as a result of the inaccessibility of the acid sites by NH₃. This is due to pore blockage by Ni nanoparticles, as well as the decrease in the number of strong acid sites, especially in Ni/HZSM-5, owing to the blockage of pores by Ni nanoparticles which makes acid sites located in those pores inaccessible to the reactants [22]. Contrariwise, the strong acid sites of the microporous and hierarchical HBEA increase after Ni deposition (Table 1 and Fig. 4B), because of an increase in the number of Lewis acid sites, arising from the interaction of surface Ni²⁺ in NiO on passivated Ni nanoparticles [64]. Furthermore, the nature of acid sites was analysed by pyridine chemisorption followed by DRIFTS (Fig. S10). Table 1 shows that the Brønsted: Lewis acid character reduces more significantly for the commercial zeolites than for the prepared hierarchical and microporous nanozeolites after doping with the Ni metal. Moreover, the Brønsted: Lewis acid ratios decrease almost by 50 % for hierarchical samples as compared to their microporous counterparts. The significant decrease in the Brønsted and Lewis acid character of the hierarchical zeolites could be due to the enhanced interaction of Ni NPs with the acidic hydroxyl groups located in the mesopore network [65].

3.1 Hydrodeoxygenation of Oleic Acid

To test the catalytic activity of the Ni incorporated on hierarchical nanozeolites and other corresponding supports, HDO of a model compound, oleic acid, was studied. A blank run of the HDO reaction without a catalyst was performed at 350 °C and 20 bar H₂ pressure to determine the effect of hydrothermal cracking. A very little amount of oleic acid was converted to hexadecanoic acid (< 1%). The majority of the product was retained as oleic acid itself (data are not shown). Apart from that, the effect of commercial zeolites H-Beta and H-ZSM-5 (5 wt.%) on the HC of oleic acid was performed to investigate the catalytic effect of support materials alone. The experiment conditions and the respective products obtained are shown in **Table S3**. The product mixture comprised unconverted oleic acid (84-93%), followed by cracked alkenes (7 – 16%) and traces of compounds such as 1-octadecanol and stearic acid (< 0.1%).

Almost all oleic acid (82.0-99.9%) is found to be converted during the wide range of reaction conditions involving supported Ni zeolite catalysts in **Table 2** (entries 1-11). In general, the prepared bifunctional zeolite doped Ni catalysts have high surface activity and Brønsted: Lewis acid ratio; thus, the oleic acid molecules can easily undergo hydrogenolysis/hydrocracking to hydrocarbons [46, 60, 66]. Notably, the microporous nanozeolite Ni/m-HBEA and its analogue hierarchical nanozeolite Ni/h-HBEA show higher oleic acid conversions of 89% and 86% due to their higher total acidities (3006 and 2823 μ molg⁻¹) and surface areas (964 and 700 m²g⁻¹) that could enhance the zeolite-metal surface-activity in hydrogenolysis of the C-O bond. On the other hand, the microporous nanozeolite Ni/m-HZSM-5 and hierarchical nanozeolite Ni/h-HZSM-5 also achieve almost similar conversions as the prepared HBEA catalysts. We anticipate that the higher ratio of Brønsted/Lewis acid characteristics (0.39 and 0.48) and narrower pores of the HZSM-5

zeolites may contribute to higher effective residence time and C-O bond fission of oleic acid [46, 67].

Similarly, the catalytic activity in terms of hydrocarbons yields of both synthesised Ni/HZSM-5 and Ni/HBEA catalysts, including hierarchical nanozeolites (Ni/h-HZSM-5 and Ni/h-HBEA) and microporous nanozeolites (Ni/m-HZSM-5 and Ni/m-HBEA) are higher than that of commercial microporous zeolites (Ni/c-HZSM-5 and Ni/c-HBEA) catalysts. For Ni/HZSM-5 catalysts, the hierarchical nanozeolite Ni/h-HZSM-5 having a higher surface area of 595 m²g⁻¹ shows 65% of total hydrocarbons yield including *n*- and *iso*- C₈-C₁₈ alkanes at 350 °C and 50 bar, which is comparable to microporous nanozeolite Ni/m-HZSM-5 (64%) and higher than commercial microporous zeolite Ni/c-HZSM-5 (49%) catalysts. Parallel trends are observed for Ni/HBEA series. Whereby, the total hydrocarbon yields are comparable for Ni/m-HBEA (69%) and Ni/h-HBEA (63%), and they are also higher than the commercial microporous Ni/c-HBEA (58%).

In this work, the individual unmodified microporous nanozeolites supported-Ni catalysts (Ni/m-HZSM-5 and Ni/m-HBEA) were relatively active as they were prepared from nanozeolites (m-HZSM-5 and m-HBEA) supports that had higher S_{BET} surface areas (**Table S1**) compared to the hierarchical nanozeolites (h-HZSM-5 and h-HBEA) and commercial microporous zeolites (c-HZSM-5 and c-HBEA). In the TEM images (**Fig. S7**), the sizes of the globular microporous nanozeolites (m-HZSM-5 and m-HBEA) are more prominent than those of hierarchical nanozeolites (h-HZSM-5 and h-HBEA). Still, they are embodied by many ultrasmall nanocrystals with a size around 10-15 nm, thereby resulting in an increase in the total surface area or surface acid activity of that material. Notably, the Ni/m-HBEA catalyst has a higher surface area even

after the incorporation of Ni metal compared to the Ni/h-HBEA catalyst, therefore producing almost similar hydrocarbon yields compared to its hierarchical counterpart.

Although higher conversions of oleic acid and hydrocarbons yields are achieved with Ni/microporous nanozeolites (Ni/m-HZSM-5 and Ni/m-HBEA), a lower nC_{18}/nC_{17} alkanes ratio is observed compared to the Ni/hierarchical nanozeolites (Ni/h-HZSM-5 and Ni/h-HBEA) (Table 2, entries 2 and 7). Using the hierarchical nanozeolite Ni/h-HZSM-5 with a higher Brønsted/Lewis acid sites ratio than Ni/m-HZSM-5 (0.48 compared to 0.39), the ratios of nC_{18}/n C17 alkanes increase from 2.9 to 3.5. The hierarchical nanozeolite Ni/h-HBEA catalyst also displays a higher ratio of nC18/nC17 alkane of 2.0 compared to its microporous counterparts, although they all have very similar Brønsted/Lewis acid ratios of around ~0.25. The HDO pathway shows a strong dependence on the Brønsted/Lewis acid ratio and mesopore structure of hierarchical materials with selectivity to C₁₈ alkane, reducing the competing route of DCO or HDC to C₁₇ alkane [6]. The correlation of the nC_{18}/nC_{17} products ratio to the Brønsted: Lewis (B/L) acid ratio is clearly shown in Fig. S11. The main reason for higher selectivity of C_{18}/C_{17} is the close proximity of Brønsted acid sites to the Ni NPs that are dispersed along the mesoporous architecture of hierarchical meso-microporous zeolites. Such proximity shows improvement in the selectivity of HDO products rather than the localization of NPs on the external surface of their typical microporous zeolites counterparts [68]. The oleic acid molecule (~2 nm) [69] has better access to the Brønsted acids located in the mesopores of hierarchical nanozeolites Ni/h-HZSM-5 and Ni/h-BEA catalysts, which are thus concluded to be more HDO selective than microporous nanozeolites [18]. Within the accepted pathway involving the fatty acid hydroprocessing: i) hydrogenolysis of the acid to the aldehyde and hydrogenation to the alcohol taking place on the nickel particles, followed by ii) dehydration at acid sites to form an unsaturated intermediate (alkene), and iii) final

hydrogenation of alkene on the nickel to produce the n- C_{18} product. The close proximity of Ni nanoparticles throughout the mesoporous structure to Brønsted acid sites could account for the improved C_{18}/C_{17} selectivity. The mesoporous hierarchical zeolite has a higher Brønsted acid sites that are accessible by the larger bulky intermediates. Therefore, the C_{18} alcohol molecules can easily undergo dehydration to an alkene intermediate, followed by hydrogenation to C_{18} alkane.

The effect of the textural property of zeolites on the nC_{18}/nC_{17} hydrocarbons ratio is systematically compared in Fig. **S12**. In general, the hierarchical pore structure does appear to contribute meaningfully to the selectivity of nC_{18}/nC_{17} , in which both h-HZSM-5 and h-HBEA hierarchical nanozeolites outperform their analogues microporous nanozeolites and commercial zeolites. The close proximity of Ni NPs throughout the mesoporous structure to acid sites could account for the improved nC_{18}/nC_{17} ratio [18]. Accordingly, in this study, the Ni incorporation in hierarchical nanozeolites h-HZSM-5 and h-HBEA resulted in a small decrease in total surface area $S_{BET} \sim 11\%$ while maintaining high total pore volume Vp and Brønsted : Lewis acid character compared to their respective analogues. In HC, the HDO route is favoured over HDC/DCO when alcohol (produced from the acid hydrogenolysis, followed by hydrogenation of aldehyde) easily dehydrates at acid sites to an alkene and then finally hydrogenates on adjacent Ni atoms to an alkane with the same carbon number as the acid [46].

The effect of temperature and pressure on the oleic acid HDO are specifically studied for hierarchical nanozeolites (Ni/h-HZSM-5 and Ni/h-HBEA) catalysts. The highest oleic acid conversions of 94-99% are achieved when the reaction is conducted at a higher temperature of 400 [°]C (**Table 2, entries 4 & 10**) or pressure of 90 bar (**Table 2, entries 3 & 8**). This indicates that the HC reaction is a temperature- and pressure dependent one [70] when using the hierarchical nanozeolites (Ni/h-HZSM-5 and Ni/h-HBEA) catalysts. In general, the liquid- and gas-phase

reactions of HC reaction have different thermodynamic characteristics. As a result, the product distribution and reaction pathway can also be varied with the alteration of reaction temperature and pressure. When a higher hydrogen pressure of 90 bar is employed, the total alkanes n- + *iso*-(C₈-C₁₈) yields for Ni/h-HZSM-5 and Ni/h-HBEA increase to 85% (**Table 2, entry 3**) and 91% (**Table 2, entry 8**), respectively. With increasing pressure from 50 to 90 bar, the ratio of nC_{18}/nC_{17} increases from 3.5 to 4.5 (**Table 2, entry 2 to 3**) and 2.0 to 4.0 (**Table 2, entry 7 to 8**) for Ni/h-HZSM-5 and Ni/h-HBEA, respectively. The high hydrogen pressure causes the rate of oleic acid hydrogenation is continuously increasing, consequently shifting the equilibrium from octadecanal to 1-octadecanol [46]. Thus, the overall HDO rate is increased with the enhanced production of n-C₁₈ while suppressing the n-C₁₇ hydrocarbon.

Contrariwise, the total yields of straight-chain alkanes decrease 14% (**Table 2, entry 4**) and 62% (**Table 2, entry 9**) at the higher reaction temperature of 400 °C for both hierarchical nanozeolites Ni/h-ZSM-5 and Ni/h-HBEA catalysts. When a reaction temperature of 400 °C and a hydrogen pressure of 90 bar is used with a Ni/h-HBEA catalyst, the yield of straight-chain alkanes decreases even further to 21% (**Table 2, entry 10**). Moreover, the selectivity towards *n*- C_{18} alkane reduces to 1.2 or less (**Table 2, entries 10 & 4**), signifying preference for HDC/DCO over the HDO route at a higher temperature. The increase in reaction temperature to 400 °C also leads to an increase in the yield of isomerised products, especially in the production of *iso*- C_{17} (7%) for Ni/h-HZSM-5 (**Table 2, entry 4**). The highest production of isomerised hydrocarbon *iso*- C_{18} (15%) is observed with Ni/h-HBEA at 350 °C, accompanied by a high hydrogen pressure of 90 bar (**Table 2, entry 8**). However, a further increase in the reaction temperature to 400 °C with a lower pressure of 50 bar reduces the production of isomerised hydrocarbon *iso*- C_{18} by two fold for Ni/h-HBEA (**Table 2, entry 9** compared to **entry 7**), which is due to the HDC reaction

pathway. In most cases, when the reaction temperature is increased, the Ni metal favours the HDC route [46]. When increasing the reaction temperature from 350 to 400 °C and decreasing pressure from 90 to 50 bar, the production of isomerised hydrocarbon *iso*-C₁₈ significantly reduces by four times from 15% to 4% (**Table 2, entry 8 compared to entry 9**), indicating a higher impact of the HDC pathway. However, a further increase in hydrogen pressure from 50 to 90 bar results in a sixfold increase in the isomerisation yield of *iso*-C₁₇, from 1 to 6% (**Table 2, entry 9 compared to entry 10**). These higher temperatures and pressure favoured not only the isomerisation of C₁₇ and C₁₈ hydrocarbons but also other smaller-range (C₈-C₁₆) hydrocarbons (**Table 2, entry 10**). The enhancement of isomerisation at 400 °C and 90 bar for Ni/h-HBEA is evidenced by a lower total hydrocarbon yield of 32%, which consists primarily of $n(C_8-C_{16})$ and n+iso (C₁₇ and C₁₈) products.

Table 2 also shows the carbon balance for most of the catalysts are from 60-93%, except for entries 4 and 10, for which the carbon balance is 22% and 32%, respectively. This is most likely due to the isomerisation of aliphatic alkanes, cracking of the heavy hydrocarbons (C_{18} and C_{17}) to light range alkanes (e.g. gasoline range) and gases such as (C_2 - C_4) at extreme temperature and pressure. GC-MS was used to identify minor products of the reaction. **Fig. S13** shows an example of a GC-MS chromatogram, and **Table S4** presents a list of detected compounds other than the main products that include compounds such as iso-paraffins (C_7 - C_{16}), naphthenes, alkyl substituted naphthenes, ethers, and alcohols.

Table 2. The liquid product composition of HC of oleic acid over Ni supported catalysts under various reaction conditions ^a

Entry	Catalyst	Т (°С)	P (bar)	Conv. (%)	Yield C8-C18 (%) ^b	Yield <i>n-</i> C17 (%)	Yield <i>iso-</i> C17 (%)	Yield <i>n-</i> C ₁₈ (%)	Yield <i>iso-</i> C ₁₈ (%)	<i>n</i> C ₁₈ / <i>n</i> C ₁₇	Carbon Balance ^c
1	Ni/m-HZSM-5	350	50	89	64	14	1	40	4	2.9	65
2	Ni/h-HZSM-5	350	50	86	65	11	1	39	7	3.5	66
3	Ni/h-HZSM-5	350	90	94	85	14	1	58	6	4.2	81
4	Ni/h-HZSM-5	400	50	99	29	0.5	7	0.3	8	0.7	22
5	Ni/c-HZSM-5	350	50	85	47	11	0.1	30	2	2.7	73
6	Ni/m-HBEA	350	50	90	69	23	3	27	6	1.2	63
7	Ni/h-HBEA	350	50	86	63	17	2	34	7	2.0	66
8	Ni/h-HBEA	350	90	98	91	13	5	54	15	4.0	91
9	Ni/h-HBEA	400	50	84	67	22	1	28	4	1.3	93
10	Ni/h-HBEA	400	90	99	32	2	6	3	5	1.2	32
11	Ni/c-HBEA	350	50	82	52	19	1	29	8	1.5	64

^a Yields and selectivity were determined based on the major products observed in the GC-FID analysis, and the reported yields and selectivity are the average of the duplicate experiments with calculated errors = $\pm 5\%$; ^b The (C₈-C₁₈) hydrocarbons yield, comprising of $n(C_8-C_{16})$ and n+iso (C₁₇ and C₁₈) products; ^c Carbon balance was calculated based on the C₈-C₁₈ liquid and gas (CO, CO₂ and CH₄) products.

Owing to the hydrotreating catalysts like Ni metal, methanation and water–gas shift reactions are among several gas-phase reactions that can occur between the deoxygenated byproducts, e.g. CO, CO₂, and H₂ [71]. The analysis of gas-phase components reveals the preference of reaction pathway (HDO or DCO/HDC) in the HC reaction (**Table 3**, entries 1-19). The HC reaction at 350 °C and 50 bar involving Ni/HZSM-5 catalysts shows a low volume of CH₄ (**Table 3**, entries 1, 2 and 5). The volume of CH₄ is slightly higher for both Ni/m-HZSM-5 and Ni/c-HZSM-5 (16%) as compared to Ni/h-HZSM-5 (14%), indicating more CO is produced via HDC in the reactions involving nanozeolite Ni/m-HZSM-5 and commercial zeolite Ni/c-HZSM-5 catalysts. The volume of CH₄ increases to 49%, when the higher hydrogen pressure of 90 bar is used (**Table 3**, entry **3**), revealing a shifting of equilibrium towards methane production [72]. Meanwhile, the catalytic performances at a higher reaction temperature of 400 °C and 50 bar show the volume of CH₄ (26%) is markedly increased, accompanied by CO₂ (24%) from the water gas shift reaction (**Table 3**, entry **4**). In the case of Ni/HBEA catalysts (**Table 3**, entries 6, 7 and 11), the CH₄ production of Ni/m-HBEA (**Table 3**, entry 6) is lower than that of Ni/h-HBEA (**Table 3**, entry 7). It is postulated that the nature of the supporting material might influence the catalytic performance of CO methanation. The development of mesoporosity provides enhanced accessibility and dispersion of active sites, leading to higher conversion rates of methanation [73]. The Ni supported on commercial microporous zeolite Beta (Ni/c-HBEA) also gives a lower amount of CH₄ (17%) (**Table 3**, entry 11). Apparently, a higher CH₄ volume (90-91%) is produced when there is an increase in the reaction temperature or pressure (**Table 3**, entries 9 & 10). Overall, the analysis of gas-phase compositions, especially in the series of Ni/HZSM-5 catalysts can serve as clear evidence for their liquid products selectivities and HC pathway.

				osition (vol. fra	ol. fraction, %)		
Entry	Catalyst	T(°C)	P(bar)	H_2	СО	CO ₂	CH4
1	Ni/m-HZSM-5	350	50	84	0	0	16
2	Ni/h-HZSM-5	350	50	86	0	0	14
3	Ni/h-HZSM-5	350	90	51	0	0	49
4	Ni/h-HZSM-5	400	50	50	0	24	26
5	Ni/c-HZSM-5	350	50	84	0	0	16
6	Ni/m-HBEA	350	50	86	7	0	7
7	Ni/h-HBEA	350	50	25	30	7	38
8	Ni/h-HBEA	350	90	61	0	0	39
9	Ni/h-HBEA	400	50	9	0	0	91
10	Ni/h-HBEA	400	90	10	0	0	90
11	Ni/c-HBEA	350	50	83	0	0	17

 Table 3. Effect of varying Ni supported catalysts and reaction condition on the gaseous product composition from HC of oleic acid ^a

^aCalculated error of products = $\pm 5\%$

The reusability study was carried out to investigate the stability of the catalyst in the HC reaction. The spent catalysts were reactivated by washing with hexane solvent and oven-dried before being used again in the reaction. In this study, the stability of Ni loaded on both nanozeolite and hierarchical nanozeolite supports, which consisted of four types of catalysts: Ni/m-HZSM-5,

Ni/h-HZSM5, Ni/m-HBEA and Ni/h-HBEA were evaluated and compared based on their best reaction conditions in the former catalytic test (Fig. 5a & b). The hierarchical Ni/h-HZSM-5 catalyst maintains a 40% hydrocarbon yield with a 1.6 ratio of nC_{18}/nC_{17} products after four consecutive runs. The recyclability results indicate that the hierarchical zeolites-supported catalysts can achieve improved chemical stability towards the coke formation during the HC reaction compared to their counterparts microporous nanozeolites. The larger nanopores centred at 62 and 83 nm of the Ni/h-HZSM-5 and Ni/h-HBEA catalysts (Fig. 2), respectively, have higher resistance towards the deposition of carbon compounds which later can transform into the coke [12, 74]. Meanwhile, Ni/h-HBEA exhibits a lower hydrocarbon yield (18%) and nC_{18}/nC_{17} ratio (1.5) after four consecutive runs. The fast deactivation of the catalyst might be owing to fast covering and/or blockage of the micropores of the Ni/h-HBEA catalyst [75]. The ratio of nC_{18} /nC17 hydrocarbons increases to 2.9 for Ni/h-HBEA in the second run but gradually decreases with the number of cycles, including for Ni/h-HZSM-5, indicating severe deactivation of Brønsted acid sites over HDC active sites (Ni atoms). In addition, the deactivation may also be correlated to the total strong acid sites of the catalyst measured at temperature >200 °C. Ni/m-HZSM-5 and Ni/m-HBEA that possess higher total strong acid sites (Table 1) are prone to deactivation in the reaction, as compared with their hierarchical nanozeolite counterparts.



Fig. 5. (a) Reusability study of the Ni/m-HZSM-5 and Ni/h- HZSM-5 catalysts towards total hydrocarbon yield at 350 °C and 50 bar; (b) Reusability study of the Ni/m-HBEA and Ni/h-HBEA catalysts towards total hydrocarbon yield at 400 °C and 50 bar.

The mass composition of the used catalyst was further characterised by TGA analysis, and the result is depicted in **Fig. S14 (a-f).** The thermogram of fresh Ni/h-HZSM-5 catalyst demonstrates no mass loss at the region of 200-600 °C (Fig. S14b). Fig. S14a shows the TGA analysis of pure stearic acid. The stearic acid was used as a reference in the TGA analysis since the presence of unconverted stearic acid was observed following the GC analysis of the product from the catalytic test of the used catalysts. The unsaturated oleic acid feedstock was able to be hydrogenated to saturated stearic acid by the active surface Ni metals, but no further hydrogenolysis is mainly instigated by the blockage [76] or oxidation of active Ni metal particles over time. **Table S4** shows pure stearic acid degrades over two ranges of broad and small decomposition temperatures of 170-330 °C and 330-500 °C [77]. Apart from the weight loss below 200 °C primarily due to the adsorbed volatile species, the fresh catalyst (Ni/h-HZSM-5) also shows a slight increment in mass from 300-500 °C. This weight increase is apparently due to the oxidation of the Ni metal [78].

Compared to the TGA and DTG curves of the used microporous nanozeolite catalysts (Ni/m-HZSM-5 and Ni/m-HBEA), hierarchical nanozeolites (Ni/h-HZSM-5 and Ni/h-HBEA) show significant mass loss steps between the above-said temperature range. The overall total weight loss of the Ni/hierarchical nanozeolites was also higher than for Ni/microporous nanozeolites catalysts (Table S5). The higher percentage of weight loss may be attributed to the more active sites of mesopores in the hierarchical catalysts and hence higher catalytic activity [78, 79]. Meanwhile, the fast deactivation of Ni/m-HZSM-5, Ni/m-HBEA and Ni/h-HBEA catalysts is due to the low tolerance to coke formation that blocks the access to the Brønsted acid sites located in the micropores [80, 81]. The micropore Brønsted acid sites deactivation is evidenced by high decomposition temperature (≥600-700 °C) and weight loss (1.24-1.84 wt.%) of coke for the abovementioned catalysts (Table S5). From our reusability study, the lifetime of hierarchical nanozeolites can be considerably prolonged from coke deposition in HC reaction. The appropriate hierarchical pore structure significantly reduces the deactivation of the catalyst by aiding in the effective diffusion of the reactant, product and coke through the mesopores [82]. In addition to this, the deactivated hierarchical catalyst can also be regenerated by properly burning off the deposited coke in an oxygen environment [83, 84]. Furthermore, the incorporation of Cu as a promoter along with Ni could reduce the coke deposition on Ni [85, 86].

Table S6 shows the catalytic HDO performances of hierarchical zeolites from the literature in comparison to ours. The HDO of stearic acid over bottom-up approach flower-like hierarchical ZSM-5 doped 20wt.% Ni showed 78% conversion of stearic acid with 69% and 9% selectivities of n+iso -C₁₈ and -C₁₇. Due to structural differences, the 12-membered ring HBEA doped 20wt.%

Ni showed lower stearic acid conversion of 70% and 61% n+iso -C₁₈ selectivity. After four recycling cycles, the flower-like hierarchically structured ZSM-5 also demonstrated a slight decline in the stearic acid conversion from 78 to 68%. [87]. Meanwhile in top-down approach synthesis [88], the dealuminated hierarchical USY supported NiMo catalyst exhibited 100% conversion of waste cooking oil with selectivity up to 30% C₁₆-C₁₈ hydrocarbons, mainly due to low acidity.

The productivity of the prepared hierarchical nanozeolites 10 wt.% Ni/h-HZSM-5 and Ni/h-HBEA compared to zeolites from the past studies is shown in Table S7. In order to effectively compare the activity of the prepared catalysts with the literature, the productivity of the catalysts is expressed in mmol of C_8 - C_{18} carbon or hydrocarbon produced. The prepared hierarchical nanozeolites show productivity of 242 and 202 mmol of C_8 - C_{18} . g Ni ⁻¹ h ⁻¹ or 3650 and 4362 mmol C_8 - C_{18} hydrocarbon g Ni⁻¹ h⁻¹. Despite almost comparable differences in overall Ni content and loading, as well as catalytic reaction conditions, the prepared hierarchical catalysts show nearly better catalytic productivity than the 5 and 10 wt.% Ni/HBEA catalysts (1011 mmol of C_8 - C_{18} g Ni ⁻¹ h ⁻¹ and 191 mmol C_{17} - C_{18} g Ni ⁻¹ h ⁻¹).

Conclusions

A novel and environmental-friendly method was developed to synthesise stable surfacesilanised and alkoxylated hierarchical nanozeolites supported Ni catalysts (Ni/h-HZSM-5 and Ni/h-HBEA). The bio-derived 1-decanol and iso-butanol solvents used in the surface alkoxylation and organosilanisation of hierarchical zeolites (h-HZSM-5 and h-HBEA) had a significant impact on the final properties, particularly in the generation of the large mesopore structure essential for many catalytic applications. The catalysts featured improved catalytic activity and selectivity towards hydrodeoxygenation in the hydroconversion of oleic acid to diesel-ranged hydrocarbons. Compared to their microporous counterparts, the Ni-doped hierarchical h-HZSM-5 and h-HBEA exhibited 86 % improvement in oleic acid conversion, and 71% and 65% enhancement in C_{18} alkane selectivity. The enhanced HDO selectivity is attributed to the interaction of strong acid sites located within the mesopores with Ni atoms. Moreover, the catalyst recyclability tests revealed that the hierarchical catalysts are more stable that microporous zeolites, thanks to their improved resistance to coking. Thus, our work indicates that the use of surface soft-templating to prepare hierarchical nanozeolites is a sustainable and advantageous method for the selective HDO reaction of bulky oxygenated compounds.

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