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ARTICLE TYPE

Hydrotreatment of renewable oils using hierarchical mesoporous H-ZSM-5 synthesized from kaolin clay†.

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Hierarchical Mesoporous ZSM-5 with tailored physicochemical properties was successfully synthesized by using kaolin clay as a cheap alumina source and organosilane as a mesopore directing agent. The synthesized material was used as a support for developing a hydroprocessing catalyst (Ni-Mo). Hydrotreatment of jatropha oil over sulfided Ni-Mo catalyst supported on the developed H-ZSM-5 was carried out. The influence of reaction conditions like temperature, pressure, LHSV were studied in detail and the results were compared with those obtained for hydrotreatment of jatropha oil using mesoporous ZSM-5 synthesized from conventional precursors. It was observed that C15-C18 hydrocarbon diesel yield was highest (93%) at temperature of 375°C, 50 bar pressure and 1.5 h⁻¹ LHSV, while the C9-C15 hydrocarbon yield (kerosene range) was maximum (37.4%) at temperature of 425°C, 80 bar pressure and 0.5 h⁻¹ LHSV. The performance of clay derived catalyst for kerosene production was comparable with that of conventional catalyst but at higher temperature. But the clay derived catalyst showed higher and more stable activity than the conventional mesoporous zeolite. This may be attributed to milder acidity (due to alumina patches), unlike conventional mesoporous zeolite which have more isolated Al sites and hence more number of acid sites.

Introduction

There has been an increasing demand for oil, rapidly increasing oil prices and uncertainties regarding petroleum availability as well as the growing concern for climate change due to the large emissions of greenhouse gases. So more and more research is directed towards renewable, sustainable and clean fuel sources.^{1,2} One of the alternatives is the production of biofuels which can be produced from plant-derived oils (triglycerides)³, specifically, non-edible and used oils such as waste restaurant oil⁴, jatropha oil⁵, algae oil⁶ etc. Since there are many advantages of biofuels such as decreased greenhouse gas emissions, decreased dependence on fossil fuels, improvement of rural economies, and increased national security⁷, therefore there is a great need for the development of more economical and feasible routes for the production of biofuels. Biodiesel production from transesterification of triglycerides is currently the primary route for production of biofuels but this route have many drawbacks, such as large quantities of glycerol produced as by-product which need to have a suitable market², lower oxidation stability, lower cetane number, engine incompatibility, poor performance in cold weather and poor emission. Another route for biofuel production is the direct hydrotreatment of non-edible triglyceride to form normal and isoalkanes of C9-C18 range hydrocarbons with much higher octane/cetane value than conventional gasoline/diesel fuel.^{2,8}

Hydroprocessing is a well-known technology in the petroleum refining industry, commonly used to crack larger molecules and/or to remove S, N and metals from petroleum derived feed stocks such as, gas oil and heavy oil.⁹ However, hydroprocessing is also very useful to produce straight chain alkanes from fatty acid triglycerides of animal fat, tall oil, and other vegetable oils, with many benefits over trans-esterification such as compatibility with current refinery infrastructure, engine compatibility, feed stock flexibility and also the resulting products with higher cetane number and low sulfur content. Jatropha looks suitable for biofuel production due to (i) its relatively fast growing nature¹⁰, (ii) it can grow in almost any wasteland without competing with arable land for food¹¹, (iii) it gives higher yield of biofuel per hectare than from canola, sunflower and soyabean.¹¹ Many studies have been reported earlier on hydroprocessing of plant oil triglycerides and their blends with gas oil over different traditional sulfided catalysts such as Ni-W/Al₂O₃, Ni-Mo/Al₂O₃ and Co-Mo/Al₂O₃, with high conversion and high deoxygenation activity which produce hydrocarbons (predominantly C15-C18 carbon range).^{1,2,4-6,12} In a study jatropha oil was hydroprocessed over trifunctional Ni-Mo/SiO₂-Al₂O₃ catalyst to produce green diesel.¹² Beside these traditional catalysts, Ni-Mo and Ni-W catalysts supported on hierarchical mesoporous ZSM-5 was reported for the hydroconversion of triglycerides of algae and jatropha oil.¹³ Among all the previous work on hydrotreatment of jatropha oil or other feedstock over various catalysts, no one targeted hydrotreatment of jatropha oil over H-ZSM-5 synthesized from kaolin clay a cheaper source of alumina, which would make this process more economical for green diesel production.

Zeolites are classified as a highly porous aluminosilicates having water/or other molecules within their pores. They are widely used in petrochemical industry as a heterogeneous catalyst for isomerisation, alkylation and aromatization process due to their unique porous properties and high degree of thermal

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stability.¹⁴ However, their small pore size limits access to relatively bulky molecules such as triglycerides. So the mesoporous zeolites with hierarchical porosity could be promising for application to catalytic conversion of bulky substrates. Therefore the synthesis of hierarchical mesoporous ZSM-5 with desirable physicochemical properties as well as good catalytic activity by using cheap raw materials like kaolin clay is challenging. Kaolin clay is a layered silicate mineral, which is composed of an octahedral alumina layer joined to a tetrahedral silica layer via shared apical oxygen¹⁵. Kaolin clay can be converted into zeolites¹⁶ using two steps (i) transformation of kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) into an amorphous and dehydroxylated but highly reactive product called metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) using metakaolinization process, (ii) hydrothermal reaction of metakaolin with conventional alkaline zeolite synthesis mixture containing organosilane as a surfactant¹⁷. Recently many groups have developed Zeolite A¹⁸, Zeolite -Y^{19,20} and ZSM-5^{16,21} from kaolin clay but the porous properties and acidities as well as catalytic properties of such materials have not been well reported. The synthesis of hierarchical mesoporous zeolites from kaolin clay is yet an unexplored area. Zeolite materials from clays, reported till date have limited applications in catalysis due to limitation of low surface area, undefined acidity and low crystallinity. Here we first time report the organosilane templated synthesis of hierarchical mesoporous ZSM-5 with tailored physicochemical properties using kaolin clay as a cheap silica and alumina source and its catalytic application in hydrotreatment of jatropa oil to produce renewable diesel and kerosene. We used this ZSM-5 as a support for developing a hydroprocessing catalyst (Ni-Mo). In our work all the vital issues like effect of calcination temperature of kaolin clay and micropore/mesopore (TPABr/ODAC) template ratio have been studied to synthesize active support for this purpose, and effect of some reaction parameter such as temperature, pressure, space velocity have also been studied for the hydroprocessing of Jatropa oil.

Experimental

Materials

Kaolin clay, tetraethylorthosilicate (TEOS), ammonium heptamolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}]$ and nickel nitrate $[\text{Ni}(\text{NO}_3)_2]$ were purchased from Sigma Aldrich. Sodium hydroxide pellets (NaOH) was purchased from S. D. Fine chemicals Ltd. India. Tetrapropyl ammonium bromide (TPABr) was purchased from Merck, India. 3-[(Trimethoxysilyl)propyl] octadecyldimethylammoniumchloride (ODAC, 60% methanol solution) was purchased from Gelest.

Preparation of Metakaolin (Metakaolinization)

Metakaolin phase is amorphous and highly reactive as compared to kaolin phase and that phase is obtained by dehydroxylation of kaolin at higher temperature. In this study we used metakaolin treated at two different temperatures (600 and 700°C for 1 h @ 10 °C/min) as alumina source.

Synthesis of mesoporous ZSM-5

The mesoporous ZSM-5 molecular sieves were synthesized hydrothermally from reaction gel containing 3-[(Trimethoxysilyl)propyl] octadecyldimethylammoniumchloride (ODAC, 60% methanol solution) as a template by following a modified recipe

of previous reported procedures^{17, 13}. A typical synthesis gel was prepared by following steps: Solution A was prepared by adding 0.4g of NaOH pellets, followed by the addition of 1.4 g of TPABr and 0.5g of metakaolin in 67.5g of distilled water under vigorous stirring at room temperature for 30 minutes until the solution was homogeneous. Final gel was obtained by adding homogenous mixture of 4.285g of TEOS and 0.595g of ODAC into solution A under vigorous stirring for next 2 h. The chemical composition of the synthesized gel was $1\text{Al}_2\text{O}_3:2.33\text{TPABr}:2.22\text{Na}_2\text{O}:11.04-11.85\text{SiO}_2:0.26-1.6\text{ODAC}:1,666\text{H}_2\text{O}$. The mixture was then transferred into a stainless steel autoclave, heated in an oven at 150 °C for 24 h. The obtained crystallized product was washed, dried at 100 °C overnight and calcined in air at 550 °C for 6 h with a heating rate of 1 °C/min. Other ZSM-5 samples were synthesized with different Si/Al ratios of 5.5, 5.6 and 5.9 by varying TPABr/ODAC ratios. Conventional hierarchical mesoporous H-ZSM-5 was prepared by similar method but using sodium aluminate and TEOS precursors with a gel composition $1\text{Al}_2\text{O}_3:10\text{TPABr}:10\text{Na}_2\text{O}:38\text{SiO}_2:1.4-4.2\text{ODAC}:7,200\text{H}_2\text{O}$.¹³ Conventional microporous zeolite with similar composition as hierarchical mesoporous H-ZSM-5 was prepared by similar method but in the absence of mesopore template (ODAC).

Metals impregnation on Supports

The hierarchical mesoporous ZSM-5 was first converted into H-ZSM-5 by ion-exchange technique taking appropriate amount of 1M NH_4NO_3 . Then the support was dried for 24 h at 110 °C and finally calcined at 550 °C in air for 6 h with a heating rate of 1 °C/min, to form H-ZSM-5. The catalysts were prepared by using conventional impregnation method taking an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and $\text{Ni}(\text{NO}_3)_2$. The support (H-ZSM-5) was mixed with the impregnation solution and after stirring for 1 h, it was dried at 100 °C and calcined in an air stream at 400 °C for 1 h with a heating rate of 1 °C/min. In the present study, the impregnation of metal was done on the highest surface area H-ZSM-5 support [MZK-C(6B)] for catalytic evaluation and the metal content was 18 wt% MoO_3 and 4 wt% NiO.

Characterization

The XRD patterns of kaolin, metakaolin and ZSM-5 samples were obtained on a Rigaku X-ray diffractometer using $\text{CuK}\alpha$ radiation operated at 40kV and 40mA. Fourier Transform Infrared (FT-IR) spectrum of kaolin and metakaolin were recorded using Perkin Elmer 1760X spectrophotometer with KBr at intensities 4000-500 cm^{-1} . The morphology studies of the samples were carried out using FEI Quanta 200 F apparatus, having tungsten filament doped with lanthanum hexaboride (LaB_6) as an x-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. The N_2 adsorption/desorption isotherms of all samples were determined at -196°C, using a BELSORP-max, Japan apparatus. All the samples were degassed at 250°C for 8 h, under vacuum before analysis. TEM images were recorded using a JEM-2000EX II microscope (JEOL) operated at 200 kV. The specific surface area (S_{BET}) of the samples were calculated by using Brunauer-Emmett-Teller (BET) method from

the linear part of the BET plot and the pore size distribution were determined from the desorption branches of isotherm using Barrett-Joyner-Halenda (BJH) method. Acidity analysis of supports were performed after they were pretreated at 350 °C for 2 h under He flow of 20 ml min⁻¹ and cooled to 100 °C. NH₃ gas was adsorbed using 10% NH₃ in Ar gas for 1 hr. The temperature programmed desorption (TPD-NH₃) studies were carried out in He stream of 30 ml min⁻¹ by increasing temperature, (at the rate of 10 °C min⁻¹) from 25 to 800 °C.

10 Catalytic Evaluation

The catalysts (6 ml) mixed with SiC (6 ml) to ensure sufficient catalyst-bed length and to improve the reaction-heat transfer, were loaded into a stainless steel tubular reactor (1.3 cm I.D and 34 cm in length) and the experiments for hydrotreatment of pure 15 jatropha oil were carried in a micro-reactor with single-zone tubular furnace, for vapor phase catalyst evaluation in continuous down-flow mode. Hydrogen pressure was controlled by a back pressure regulator, gas flow was controlled by a mass flow controller (Brooks), catalyst bed temperatures were controlled by 20 temperature controllers and registered by two thermocouples, one for skin temperature and one for heart (catalyst bed) temperature. A high pressure liquid metering pump (Eldex) was used to maintain desired liquid flow. The main feedstock is mixed with high pressure hydrogen before entering into the reactor where the feed molecules undergo hydroprocessing. After the reaction, the 25 gas-liquid reaction mixture were passed through the high pressure gas-liquid separator to separate gaseous fraction (containing hydrogen with small quantities of CO, CO₂, propane and other lighter hydrocarbons) from hydroprocessed effluent. Gaseous 30 products were released to a gas-meter. Liquid products were analyzed by GC.

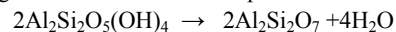
The catalysts were presulfided using a mixture of dimethyl disulfide and gas oil at atmospheric pressure and 350 °C for 9h. The reaction conditions for all the catalytic hydrotreating 35 experiments were varied as follows: temperature 350-425 °C, pressure 50 and 80 bar, LHSV 0.5-1.5 h⁻¹ and H₂ to feed ratio of 1500 ml/ml. We analyzed the liquid products thrice during stabilization period by GC to monitor constant activity, stabilization of process parameters were also confirmed in terms 40 of reactor hydrogen pressure, temperature as well as hydrogen and liquid flow. Two samples were collected at each reaction condition and analyzed by GC for constant activity to ensure that there was no observable catalyst deactivation during an experiment. Liquid feed compositions and product samples were 45 analyzed with Varian 3800-GC using CP-Sil Pona CB column for detailed hydrocarbon analysis (ASTM D5134-9), vf-5ms column for hydrocarbons, free fatty acids, triglycerides and Varian Select TM Biodiesel column for free fatty acids, triglycerides. The composition of jatropha oil used in this study is 50 C16:0/C16:1/C18:0/C18:1/C18:2/C18:3/C20:0= 15.1/1.0/7.1/42.2/34.1/0.2/0.2.

Results and discussion

Metakaolinization and Catalyst Characterization

XRD patterns of kaolin clay and metakaolin calcined at 600 °C 55 (MKR-600) and 700 °C (MKR -700) are shown in Fig. S1 (ES1†) which represents the characteristic peaks of kaolin clay and amorphous nature of metakaolin. Metakaolin is obtained by the

calcination of kaolin at temperature between ~ 550°-950 °C and this transformation (or dehydroxylation) of kaolin into 60 metakaolin is known as metakaolinization and during this the following chemical reaction takes place²².



In metakaolinization, kaolin loses its structural water with a reorganization of the structure, only a small part of the AlO₆ 65 octahedra is maintained while the rest are transformed into much more reactive tetra and penta coordinated units²³ and at very higher temperature mullite and cristobalite phases are obtained.²⁴ In this work metakaolins obtained after the calcination of kaolin

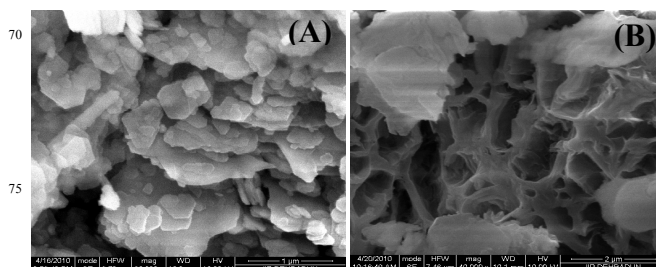


Fig.1 SEM pictures of (A) kaolin clay, (B) MZK-C (6B).

at 600 °C and 700 °C for 1h were used. The reason for choosing 80 only two types of metakaolin is that when the calcination temperature increases to 700 °C, the number of active aluminium sites is reported to a maximum and after 700 °C the number of active aluminium sites decrease slowly¹⁵. Fig. S2 (ES2†) 85 represents the FTIR spectra of metakaolins calcined at 600 °C and 700 °C respectively, showing the characteristic bands of metakaolin^{15,25}, which are centred at about 1100, 820, 465 cm⁻¹. The Si-O-Si stretching band appeared at 1078-1090 cm⁻¹ showing the characteristic vibration band for tetrahedral sheet of 90 silica. The other bands near 820 and 465 cm⁻¹ represent unconverted free silica and/or quartz present in the sample and Si-O-Si and Si-O-Al bending bonds, respectively, which were

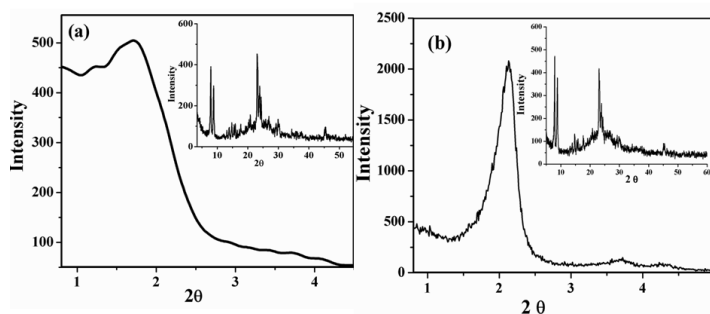


Fig. 2 Low angle and wide angle (insets) X-ray diffraction pattern of ZSM-5 95 samples prepared with: (a) high TPABr/ODAC template ratio [MZK-C(6A)]; (b) low TPABr/ODAC template ratio i.e., [MZK-C(6B)]

almost not effected by increasing calcinations temperature^{15,25}.

Fig. 1A and B represent the SEM images of parent kaolin clay 100 and synthesized mesoporous ZSM-5 sample MZK-C(6B), respectively. Fig. 1 (A) clearly shows that kaolin clay has small pseudohexagonal particles (or plate like particles) of < 1µm size²⁶, while SEM image of MZK-C(6B) (Fig. 1B) indicates its sponge like morphology with reticulate networks and macroporous structure. Such morphology is expected to be 105

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favourable for better diffusion of bulky molecules and slower deactivation due to slow coke accumulation.

The XRD patterns of the mesoporous ZSM-5 samples show the typical low angle XRD (100) reflection in the range $2\theta = 1-2^\circ$ due to the mesoporous structure along with pure zeolite peaks in wide-angle (Fig. 2a and b). The sample prepared at high TPABr/ODAC template ratio (4.75) showed a broad mesoporous hump and sharp crystalline zeolite peaks, due to zeolitic structure crystallization being more favoured (Fig. 2a) but, the sample

Table 1. Physicochemical properties of ZSM-5 samples synthesized from kaolin and mesoporous ZSM-5 synthesized by conventional method.

Sample Name	TPABr/ODAC ratio	S_{BET} (m^2g^{-1})	Pore Volume (cm^3g^{-1})	Mean Pore Diameter (nm)	Micropore Volume (cm^3g^{-1})	Mesopore Volume (cm^3g^{-1})	Si/Al ratio	Relative Crystallinity (%)
MZK-C(5A) ^a	8.96	272 (58)	0.22	3.3	0.10	0.12	5.5	-
MZK-C(5B) ^a	4.75	290 (70)	0.24	3.2	0.10	0.14	5.6	-
MZK-C(5C) ^a	1.46	464 (213)	0.47	4.0	0.11	0.36	5.9	-
MZK-C(6A) ^b	4.75	312 (79)	0.29	3.7	0.12	0.17	5.6	30
MZK-C(6B)^b	1.46	566 (234)	0.53	3.8	0.17	0.36	5.9	40
Meso-ZSM-5 (L)	7.1	475 (134)	0.42	3.6	0.19	0.23	19	100
Meso-ZSM-5 (H)	2.4	940 (409)	0.42	3.8	0.17	0.25	19	30

^aKaolin calcined at 600 °C, ^bKaolin calcined at 700 °C, Micropore area is in the parentheses.

Table 2. Acidities of H-ZSM-5 samples MZK-C(6A) and MZK-C(6B) synthesized using metakaolin and mesoporous H-ZSM-5 synthesized by conventional method.

Sample Name	Total Acidity (mmol NH ₃ /g Cat.)	Acid Strength dist. (mmol NH ₃ /g Cat.)		
		Strong	Medium	Weak
MZK-C(6A) ^b	0.3	0.1	0.1	0.1
MZK-C(6B) ^b	0.3	0.1	0.1	0.1
Meso-H-ZSM-5(L)	0.4	0.1	0.1	0.2
Meso-H-ZSM-5(H)	0.4	0.2	0.1	0.1

^bKaolin calcined at 700 °C.

prepared at low TPABr/ODAC template ratio (1.46) (Fig. 2b) showed a sharp mesoporous peak but low-intensity broad semi-crystalline zeolite peaks, due to mesoporous structure crystallization being more favoured. Increasing Si/Al ratio in the synthesis gel did not improve the crystallinity of the material.

Effect of TPABr/ODAC template ratio and metakaolinization temperature on physicochemical properties

Table 1 show the physicochemical properties of H-ZSM-5 supports, which were synthesized by using two different types of metakaolinized clay with different TPABr/ODAC template ratio and compared with conventional mesoporous ZSM-5 (meso-ZSM-5). From Table 1, it is clear that among the synthesized H-ZSM-5 supports (MZK-C) from metakaolin, sample prepared at higher metakaolinization temperature and with lower TPABr/ODAC template ratio [MZK-C(6B)] has the highest surface area and pore volume. Increasing Si/Al ratio in the samples by increasing the amount of added external Si source in the synthesis gel did not improve the porosity of the material. The acidity of the H-ZSM-5 supports synthesized using kaolin (MZK-C) was slightly lower than those synthesized using conventional

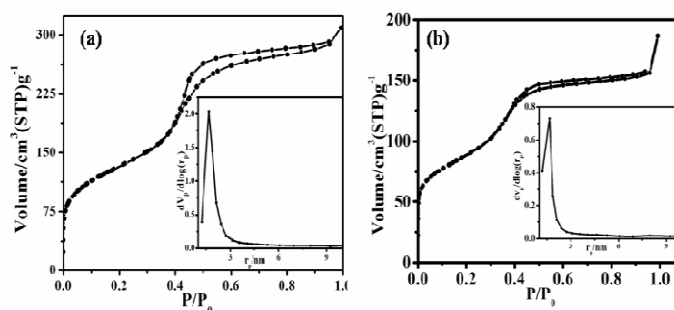


Fig. 3 N₂ sorption and BJH curves (insets) of (a) MZK-C (6A), (b) MZK-C (6B)

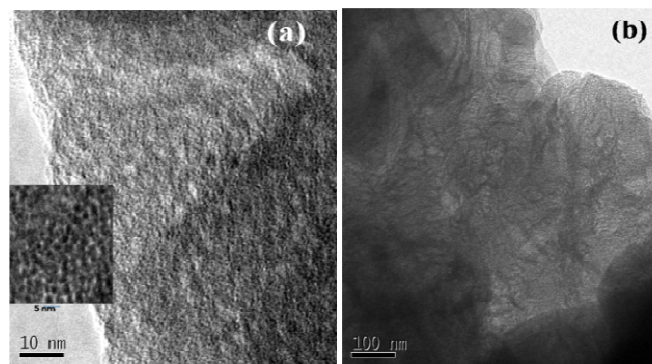


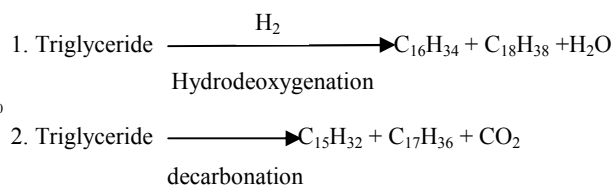
Fig. 4 HRTEM images of ZSM-5 sample MZK-C (6B): (a) plane view, (b) Cross-sectional view.

precursors (Meso-H-ZSM-5), which is shown in Table 2. The distribution of acid sites of different strengths was similar for the samples synthesized using kaolin. Most of the Al in these samples are expected to be present as alumina patches with very low acidity. Isolated Al sites which are generally responsible for acidity are expected to be lower than conventional ZSM-5 because kaolin structure has alumina sheets which are not being broken completely during synthesis, while for traditional ZSM-5, precursors with isolated Si and Al are used to prepare the structure resulting in more homogeneous dispersion of Al and Si in aluminosilicate framework leading to more number of isolated Al sites in traditional zeolites. Nitrogen sorption studies (Fig. 3 i and ii) showed a type IV isotherms typical for mesoporous materials with a clear step ($P/P_0 = 0.4-0.8$) and narrow pore size distribution (Fig. 3 insets). In comparison microporous H-ZSM-5 zeolites have higher micropore surface area ($385 m^2g^{-1}$), but very low pore volume ($0.13 cm^3g^{-1}$) and very low mesopore area ($82 m^2g^{-1}$) with small pore size ($<1 nm$). Very low mesoporosity in this material restricts its application to processing bulky feeds. In Fig. 4, TEM analysis clearly show mesopores without any phase-separation or pore blockage. It is clearly seen from Figure 4b that the mesoporosity is present in the material over a long range (micrometer range), with clear pores and it can be inferred that the synthesized H-ZSM-5 material has high degree of framework confined mesoporosity. Both plane view and cross-sectional view show that all the kaolin material has been effectively converted into mesoporous structure. But presence of alumina patches and isolated extra-framework Al cannot be ruled out as also observed for such samples in ²⁷Al MAS-NMR.¹³ Strong acidity (~33%) from NH₃ TPD studies (table 2), which is generally attributed to extra framework Al (Lewis acid sites) including those interacting

with Brønsted acid sites, as also reported earlier for kaolin free hierarchical mesoporous H-ZSM-5.¹³ Alumina patches in kaolin derived samples are probably responsible for lower acidity of these samples. We reported earlier¹³ that sample Meso-ZSM-5(L) has lower extra-framework Al than Meso-ZSM-5(H), which could be the reason for lower fraction of strong acid sites.

Hydrotreatment of Jatropha oil over Ni-Mo H-ZSM-5

Jatropha oil mainly contains triglyceride molecules with C16 and C18 hydrocarbon chains in which ~73% are unsaturated C18 hydrocarbon chains. The main reactions involved during hydroprocessing of jatropha oil are saturation of unsaturated hydrocarbon chains followed by hydrodeoxygenation (hydrogen addition pathway) and decarbonation (carbon removal pathway) for the removal of the oxygen atom and further hydrocracking¹³.



Comparison of Catalytic performance

A comparative study of hydroconversion of jatropha oil over various catalysts has been shown in table 3. Comparison of the catalytic performance of kaolin derived H-ZSM-5 support was made with the catalysts supported on alumina, silica-alumina (Si/Al=1.1) and kaolin free hierarchical mesoporous H-ZSM-5 (Si/Al=19). Alumina and silica-alumina supported catalysts are more selective towards C15-C18 hydrocarbons (diesel) production, at similar conversions as those obtained over kaolin derived catalyst support. Mesoporous Ni-Mo/Alumina is most suitable for diesel production. Kaolin free H-ZSM-5 supported

Table 3. Comparative study of hydroconversion of jatropha oil over various catalysts

Catalyst	T (°C)	P (bar)	LHSV (hr ⁻¹)	Yield (C9-C15)	%Yield (C15-C18)	%Conv.	Time (hr.)	Ref.
Ni-Mo/H-ZSM-5 [MZK-C(6B)]	375	50	1.5	10.85	93.6	>99	120	This work
Ni-Mo/H-ZSM-5 [MZK-C(6B)]	425	80	0.5	37.5	54.2	>99	120	This work
Ni-Mo/H-ZSM-5 (L)	380	80	1	42.7	48.1	96	48	13
Ni-Mo/H-ZSM-5 (H)	410	50	1	54.3	42.2	96	48	13
Ni-Mo/Al ₂ O ₃	360	50	1	<1	94.9	100	120	2
Ni-Mo/SiO ₂ -Al ₂ O ₃	380	50	2	<1	96.4	>99	120	32

catalyst showed slightly lower conversion (3-4% lower) at optimum reaction conditions and deactivated faster, than kaolin derived H-ZSM-5 supported catalyst. Better activity and slower deactivation of kaolin derived H-ZSM-5 sample may be

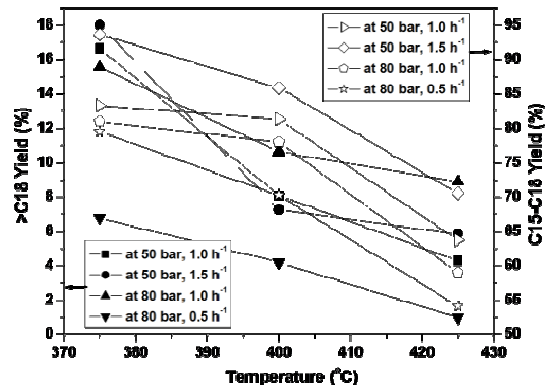


Fig. 5 >C18 and C15-C18 yields (%) in product obtained after hydroconversion of Jatropha oil over NiMo/H-ZSM-5 [MZK-C(6B)].

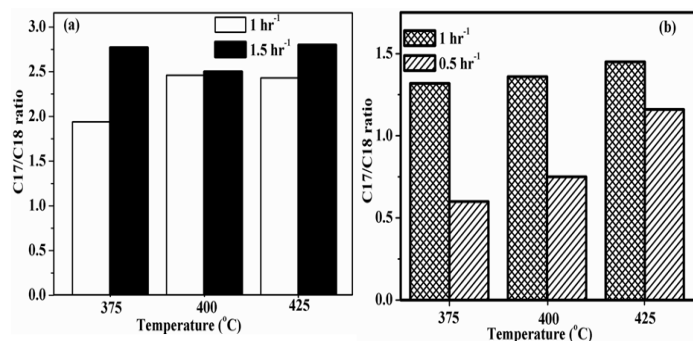


Fig. 6 C17/C18 ratio for (a) 50 bar; (b) 80 bar.

attributed to its sponge like morphology with reticulate networks and macroporous structure (SEM, Fig. 1B) which is expected to be favourable, for better diffusion of bulky triglyceride reactant molecules, and slower deactivation due to slow coke accumulation. Such macroporosity was not observed in case of kaolin free hierarchical mesoporous H-ZSM-5. It must be mentioned here that conventional non-mesoporous (microporous) zeolites show poor activity (<20 % conversion) and deactivate rapidly because the micropores are inaccessible to triglycerides, as also reported earlier¹³. Thus, kaolin derived H-ZSM-5 performs better than kaolin free H-ZSM-5 in terms of activity and stability but at higher temperature. Faster deactivation of high Si/Al ratio ZSM-5 samples than that for alumina or low Si/Al ratio (1.1) silica-alumina supported catalyst (table 3) was the reason for keeping Si/Al ratio low in these clay derived zeolites. Combined properties of alumina patches with low acidity, along with moderate acidity of zeolite probably leads to slower deactivation, while rapid deactivation is observed with low Al content (higher acidity) zeolites. Further improving the catalyst by fine-tuning the acidity (Si/Al ratio), by post-synthesis methods, may help in improving the kerosene yield and lower the operation temperature.

Effects of process parameters on yield of various products are discussed below.

Diesel range (C15-C18) product yield

Fig. 5 show the results for C15-C18 and >C18 hydrocarbon yield from hydrotreatment of jatropha oil over Ni-Mo catalyst at different reaction conditions such as temperature (375 °C to 425

°C), pressure (50 and 80 bar) and space velocities (0.5 -1.5 h⁻¹). We observed nearly complete conversion of triglycerides (>99%) at these reaction conditions. At milder reaction conditions like 375 °C temperature, 50 bar pressure and 1.5 h⁻¹ space velocity the C15-C18 product yield was higher (about 93%) but the yield decreased to 83% at same reaction conditions but with lower reaction temperature at same pressure and space velocity which indicates that the diesel range hydrocarbons (deoxygenation products) are hydrocracked into smaller molecules at higher temperature. The diesel range product yield was slightly lowered when the pressure was increased from 50 to 80 bar at all reaction temperature, and minimum diesel range product yield was 54 % at 425 °C, 80 bar and 0.5 h⁻¹.

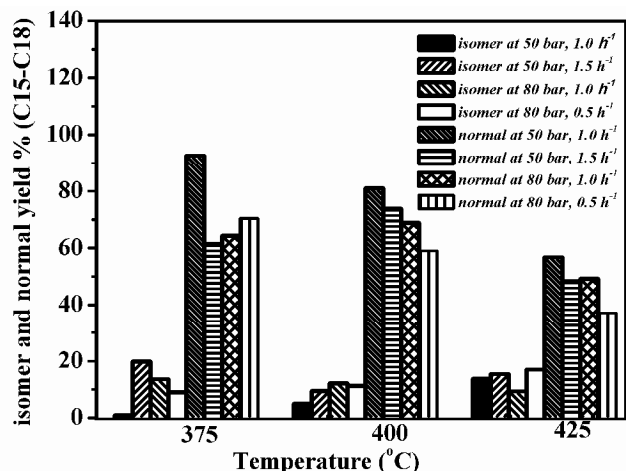


Fig. 7 Isomer and normal yield (%) of C15-C18 in product obtained after hydroconversion of Jatropha oil over NiMo/H-ZSM-5 [MZK-C(6B)].

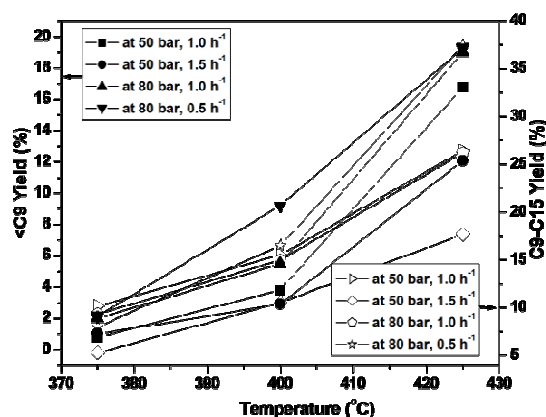


Fig. 8 C9-C15 and <C9 yields (%) in product obtained after hydroconversion of Jatropha oil over NiMo/H-ZSM-5 [MZK-C(6B)].

If we look at the yield (%) of > C18 product, it observed that the yield was maximum (18%) at lower temperature (375 °C), lower pressure (50 bar) and higher space velocity (1.5 h⁻¹), due to the formation of oligomerized product. The yield of these products was minimized (<1%) at higher temperature (425 °C), higher pressure (80 bar) and lower space velocity (0.5 h⁻¹). The >C18 products are the oligomeric products as identified and discussed in earlier studies.²⁹⁻³¹

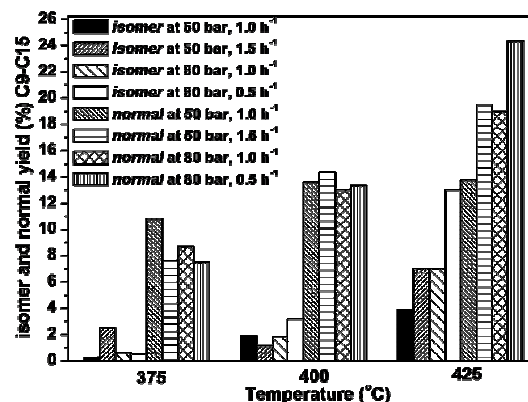


Fig. 9 Isomer and normal hydrocarbon yield (%) of C9-C15 in product obtained after hydroconversion of Jatropha oil over NiMo/H-ZSM-5 [MZK-C(6B)].

The distribution of hydrocarbons in the products is affected by the oxygen elimination pathway.^{2, 27-28} Hydrocarbons with one carbon atom less than the original fatty acid chain i.e. C17 and C15 alkanes are formed from triglyceride by decarbonation (with CO₂ as the side-product) while, C18 and C16 alkanes with the same number of carbon atoms as in the corresponding fatty acid chain, are the products of hydrodeoxygenation reaction (with hydrogen addition and water as the side-product). The extent of both pathways are dependent on reaction conditions, and can be consequently elucidated from the liquid hydrocarbon distributions. The C17/C18 ratio of major product alkanes i.e. n-heptadecane (C17) and n-octadecane (C18), can be taken as a measure of relative ratio of decarbonation (C17) versus hydrodeoxygenation (C18) and the results are shown in Figs. 6(a) and (b), respectively. From Fig. 6(a) it is clear that decarbonation route is more favoured at all temperatures and 50 bar pressure. At 80 bar pressure (Fig. 6b) too the decarbonation route is more favoured at all temperatures and 1 h⁻¹ LHSV. Hydrodeoxygenation route is more favoured (C17/C18<1) only at 0.5 h⁻¹ and 380°C, 400°C. Thus, comparing Figs. 6a and b, decarbonation pathway (which is desirable, as it does not require hydrogen addition), is most favoured at lower pressure of 50 bar and higher space-velocity of 1.5 h⁻¹ at all reaction temperatures 380°C - 425°C.

Influence of temperature on the yields of C15-C18 normal hydrocarbons and their isomers at different pressures and space velocities are shown in Fig. 7. Higher space velocity (1.5 h⁻¹) and higher pressure (80 bar) is favourable for improving the isomers yield at lower reaction temperature of 375°C. At higher temperatures (400°C, 425°C), the influence of pressure (50 bar, 80 bar) and space velocity (0.5-1.5h⁻¹) is not significant. Temperature also affects the isomer yield of C15-C18 range product and at highest reaction temperature (425 °C), maximum yield of isomers was obtained and which is due to the more cracking and isomerization of larger molecules.

Kerosene range (C9-C15) product yield

Fig. 8 show the kerosene range hydrocarbon (C9-C15) and <C9 hydrocarbon product yield from hydrotreatment of jatropha oil over Ni-Mo catalyst at different reaction conditions such as temperature (375 °C to 425 °C), pressure (50 and 80 bar) and

space velocities ($0.5 - 1.5 \text{ h}^{-1}$). Kerosene yield increases with increasing temperature and the yield was maximum after reaching higher temperature of $425 \text{ }^\circ\text{C}$. It is expected that hydrocracking pathway is favoured with increasing temperature and larger molecules are cracked into smaller ones. The trend was same at all reaction pressures ranging from 50 to 80 bar. The maximum kerosene range hydrocarbon (C9-C15) yield varied between 17-38 % (at $425 \text{ }^\circ\text{C}$) at different reaction conditions (50, 80 bar pressure and $0.5-1.5 \text{ h}^{-1}$ space velocity).

The yield of light (<C9) hydrocarbons also shows same trend as kerosene range hydrocarbon products. The Yield of <C9 hydrocarbon increases with increasing the temperature and is maximum (18 %) at higher temperature ($425 \text{ }^\circ\text{C}$), pressure (80 bar) and lower space velocity (0.5 h^{-1}). Fig. 9 shows the isomer and normal hydrocarbon yield of kerosene range product, which clearly shows that the yield of isomers and normal hydrocarbons increases with increasing the temperature which is due to more cracking and isomerization of larger molecules at higher temperatures. No clear trend is observed in the influence of pressure (50 bar, 80 bar) and space velocity ($0.5-1.5 \text{ h}^{-1}$) on the isomer yield. Comparing Figs. 7 and 9, it is observed that as the yield of kerosene range hydrocarbons increases with temperature, the yield of diesel range hydrocarbons decreases, due to cracking of the latter into former.

Life of catalyst

To investigate the catalyst life and the effect of the reaction time,

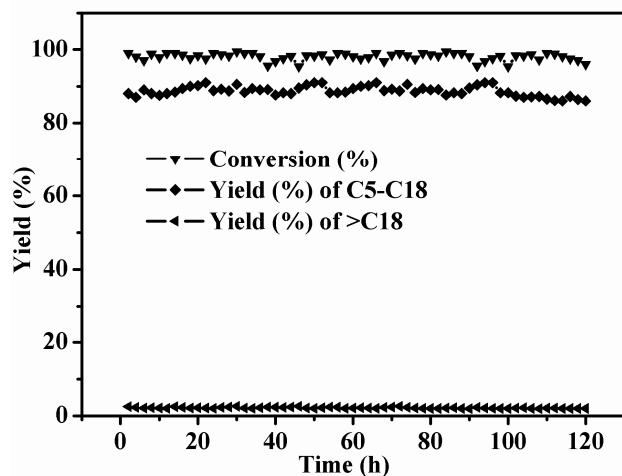


Fig. 10 Life of the catalyst Ni Mo/H-ZSM-5 [MZK-C(6B)] at 80 bar, 0.5 h^{-1} LHSV and $425 \text{ }^\circ\text{C}$.

long experiment run of 120 h was conducted over Ni-Mo/H-ZSM-5 catalyst at the condition of 0.5 h^{-1} , 80 bar and $425 \text{ }^\circ\text{C}$. Results show that no activity loss with reaction time and no observable change in the colour of product was observed. Liquid hydrocarbon (C5-C18) yield also remained constant (Fig. 10).

Conclusions

Hierarchical mesoporous ZSM-5 was successfully synthesized by using kaolin clay and organosilane as a mesopore template. The results suggest that lower ratio of templates used for micropores and mesopores, respectively, and higher metakaolinization temperature ($700 \text{ }^\circ\text{C}$) are favourable conditions in enhancing the

physicochemical properties of ZSM-5. Jatropha oil could be converted into liquid hydrocarbons over sulfided Ni-Mo catalyst using these clay derived hierarchical mesoporous ZSM-5 as support, with high yield (93%) of C15-C18 (diesel) range hydrocarbons. The kerosene range (C9-C15) hydrocarbons could also be obtained over the developed Ni-Mo catalyst with good yield (37.4%) at optimized conditions. It is also observed that depending on the reaction conditions, the oxygen removal pathway from triglyceride molecule was predominantly decarbonation route or hydrodeoxygenation route. So the use of kaolin clay, as a precursor in the synthesis of hierarchical mesoporous ZSM-5, and its use for hydrotreatment of jatropha oil glycerides, and further improvements in the catalyst (such as by fine-tuning acidity), may make this an economical process to produce kerosene, with stable performance.

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