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# ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



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Monometallic and bimetallic Ni<sub>2</sub>P, MoP, and NiMoP active species were successfully impregnated on thermally stable, high surface area mesoporous alumino-silicate with Si/Al 10 ratio, at room temperature by a facile wet impregnation method under both acidic and basic medium, using HCl and NH<sub>4</sub>OH as pH regulators. The intrinsic role of pH in altering the physicochemical properties of the catalysts was comprehensively evaluated. The catalysts were tested in a high-pressure stainless steel fixed fed reactor, at different temperatures ranging from 275-350°C, under 10-40 bar hydrogen pressure for hydrodeoxygenation (HDO) of methyl heptanoate. The reaction pathway and product distribution of methyl heptanoate is manifested at different temperature and pressure. HDO activity and synergetic factor were found to be remarkably higher for NiMoP/MAS (10)-A catalyst than NiMoP/MAS (10)-B catalyst or its monometallic counterparts. This investigation proves that NiMoP/MAS (10)-A catalyst can potentially be a promising catalyst for green fuel production from non-edible oils through hydrodeoxygenation. It was also unequivocally confirmed that the catalytic process did not suffer from any mass transfer resistance thus making the scale-up process of the reaction more feasible.

# Introduction

The rapid depletion of conventional fossil fuels leading to inevitable fossil fuel shortage and degradation of the ecosystem owing to the constant excessive use of nonrenewable fossil fuels are the two pivotal reasons, that has made exploring of alternative resources an urgent need of the hour. Use of non-edible oils obtained from biomass to produce fuel precursors and fuel components is one such alternative resource. However, the most significant step towards the generation of a greener and a more secured energy for future is the development of an efficient catalyst paving the way for an efficient process. Such development could be an antidote to the challenges faced by the industries associated with fuel production <sup>[1]</sup>. The high oxygen content present in bio-oil limits its direct usage as a fuel, since it possesses deleterious properties such as poor heating value, thermal instability, nonvolatility, high viscosity, and immiscibility with fossil fuels; hence bio-oil up gradation process becomes essential and inevitable in order to upgrade its quality as a fuel<sup>[2]</sup>.

Department of Chemistry, Anna University, Chennai-600025, Tamil Nadu, India \* Corresponding Author: K. Shanthi (shanthiramesh@annauniv.edu.in) † Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x Conventional catalytic hydrotreatment process is one of the most adopted processes to remove the oxygen content from naturally available bio-oils <sup>[3, 4]</sup>. Numerous reports have been published for hydrodeoxygenation (HDO) of non-edible oils <sup>[5-6]</sup>. Methyl heptanoate, a simple ester of triglycerides present in all the non-edible oils is essentially subjected to hydrocarbon fuel upgradation via catalytic transformation; this is an emerging field and the development of an efficient catalyst for the HDO pathway is being vehemently explored <sup>[7]</sup>.

Hydrotreating catalysts owning transition metal compounds have shown excellent selectivity and conversion towards the removal of nitrogen and sulfur atoms from crude oil <sup>[8, 9]</sup>. Particularly, y-alumina supported Ni-Mo catalyst has been extensively used as a hydrotreating catalyst in oilrefineries <sup>[10]</sup>. Even though gas phase preparation of Ni-Mo sulfide catalyst is highly active, they are found to be thermodynamically less stable and the unreacted sulfur molecules existing at high temperature poses a great threat to the eco-system <sup>[11]</sup>. In order to overcome these drawbacks, metal catalysts have been recently prepared in the phosphide form, which not only is more stable and highly active but also retains its structure after prolonged use [12]. The superior textural properties, thermal stability and acidity possessed by the metal phosphide catalysts have been found responsible for significant enhancement of activity of the catalysts <sup>[13]</sup>. It is reported that transitions metal phosphides Mo/P, WP, Fe<sub>2</sub>P,

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Co<sub>2</sub>P, and Ni<sub>2</sub>P showed excellent catalytic activity towards HDO of lignin model compounds <sup>[14-15]</sup>. Ni as a promoter for Mo based catalyst and introduction of phosphorous to Ni promoted catalysts; both have been reported to play a significant role in enhancing the efficacy of the catalyst <sup>[15]</sup>. Ni<sub>2</sub>P has been reported to be an active component for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodechlorination types of reactions with superior catalytic activity <sup>[16-17]</sup>.

Even though Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub> supported Ni-Mo catalysts have been used for HDO of esters, phenolics, cyclic ketones and aldehydes <sup>[17-18]</sup>, there is still demand for development of new supports with improved textural property, morphology and thermal stability <sup>[19]</sup>. Mesoporous silica has been widely used as support for Ni-Mo catalysts with improved textural properties, homogeneously dispersed active species and increased acidity <sup>[20]</sup>. Various mesoporous silicates such as MCM-41, HMS, SBA-15 and KIT-6 have been widely used as supports in hydrotreating catalysts <sup>[8, 21]</sup>. However, the preparation of alumino-silicates with low Si/Al ratio is tedious due to the difficulty in incorporating aluminium into the mesoporous silica framework by employing one-pot hydrothermal method <sup>[22-23]</sup>.

The preparation of Ni<sub>2</sub>P, MoP, and NiMoP based catalysts have been reported by wet impregnation, temperature programmed reduction, and sequential pore-filling impregnation methods <sup>[10, 24-25]</sup>. The catalysts synthesized by these reported methods when scaled up from pilot to industrial reaction conditions, suffered from a major drawback of structural instability caused by the conversion of the active metals into their respective oxide forms in the long run. In order to overcome this flaw, the intrinsic role of pH in the catalysts synthesis thereby affecting the physicochemical properties and the catalytic activity of the catalysts has been comprehensively evaluated and it was observed that under optimized pH values the synthesized catalysts possessed improved textural properties and excellent structural stability <sup>[18]</sup>.

In this present work, two vital aspects pertaining to 41 the catalytic hydrotreating of non-edible oil based model 42 compound that was focused upon were, synthesizing 43 structurally stable material by employing a simple preparation 44 method and seeking an efficient and energy economical 45 catalyst for low-temperature HDO reaction. Along the same 46 lines, MAS (10) with high specific surface area was synthesized 47 by a simple sol-gel method at room temperature. The effective 48 formation of Ni<sub>2</sub>P, MoP, NiMoP catalysts over the MAS (10) 49 support was controlled by acidic and basic medium using HCl 50 and  $NH_4OH$  respectively. The effect of pH on the 51 physiochemical properties and the catalytic activity of the 52 catalysts, synergistic factor in bimetallic catalysts, the product 53 distribution and the reaction pathways in hydrodeoxygenation 54 were all comprehensively evaluated. Each catalyst was tested 55 under long term experimental conditions incorporated in the 56 high pressure fixed bed vapour phase reactor; under optimized 57 reaction parameters and the structural-activity relationship of 58 the catalysts were also evaluated. 59

# Experimental

#### Materials

Tetraethylorthosilicate (TEOS), methyl heptanoate, cetyltrimethylammonium bromide (CTAB), nickel nitrate hexahydrate, ammonium heptamolybdate, ammonium dihydrogen phosphate, aluminium nitrate were obtained from Merck. m-Xylene, and hydrochloric acid (35-38%) were purchased from S.D fine chemicals. Polyethylene glycol Mw-4000 (PEG-4000) was purchased from molychem. Solvents such as methanol, acetone, ethanol and other chemicals were used as such without any further purification.

#### Synthesis of mesoporous alumino-silicate (MAS)

Mesoporous alumino-silicate (MAS) was synthesized using PEG-4000 as particle size regulator and CTAB as structure directing agent at room temperature (RT) based on a procedure reported by Zhai et al <sup>[21]</sup>. After homogenizing the surfactant solution mixture, calculated amount of TEOS and Al (NO<sub>3</sub>)<sub>3</sub> with Si/Al=10 ratio were slowly added to the above reaction mixture, maintained at pH 9.0 by using 25% NH<sub>4</sub>OH solution. Then, the reaction mixture was continuously stirred for 2 days at room temperature. The obtained solid product was filtered, washed well with doubly distilled water (DD) and dried at 80°C for 24 h. The dried material was calcined at 550°C for 6 h. The sample was denoted as MAS (10).

#### Catalysts preparation

Ni<sub>2</sub>P, MoP and NiMoP/MAS (10) catalysts were synthesized by wet impregnation method on the basis of previously reported literature by employing acidic as well as basic medium <sup>[24]</sup>. Nickel nitrate, ammonium heptamolybdate and ammonium dihydrogen phosphate were used as nickel, molybdenum, and phosphorus precursors respectively. Metal precursor solution was prepared using the following ratios Ni/P = 0.3, P/Mo = 0.06 and Ni/Mo = 0.2 dissolved in DD water for NiP, MoP and NiMoP active-metal composites respectively. The prepared precursor solution was added to the already synthesized MAS (10) support under acidic (35% of HCl) and basic (25% of aqueous ammonia) medium and stirred using a stirrer. Ni-MoP catalyst is pale green. Ni<sub>2</sub>P and MoP are in white colour in both acidic and basic medium. All the prepared materials were washed with water, dried in vacuum followed by temperature programmed reduction up to  $650^{\circ}$ C under H<sub>2</sub> atmosphere for 6 h. The catalysts were designated as Ni<sub>2</sub>P/MAS (10)-A, MoP/MAS (10)-A, MoP/MAS (10)-B, NiMoP/MAS (10)-A and NiMoP/MAS (10)-B wherein A & B denote the acidic and basic condition adopted in the synthesis respectively.

#### Materials characterization

All the synthesized catalysts were characterized by various physicochemical techniques. The diffraction pattern of the samples was recorded using BRUCKER D8 diffractometer in the range of  $0.5-5^{\circ}$  and  $10-80^{\circ}$  20 values with step scan rate of

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DOI: 10.1039/C8NJ05145C

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0.2 deg/min using Cu K $\lambda$  as the radiation source ( $\lambda$ =1.548 Å). N<sub>2</sub> sorption isotherms were obtained using QUADRASORB SI automatic analyzer at liquid N<sub>2</sub> temperature. H<sub>2</sub>-Temperature Programmed Reduction (H<sub>2</sub>-TPR) and NH<sub>3</sub>-Temperature Programmed Desorption (NH<sub>3</sub>-TPD) studies were carried out with QUADRASORB SI. NH<sub>3</sub>-TPD/H<sub>2</sub>-TPR by using 5%H<sub>2</sub>/95%Ar and 10%NH<sub>3</sub>/90%He gas mixtures respectively. Before the TPD/TPR analysis, 0.05 g of sample was pre-treated at 400 °C for 2 h under helium flow (80 mL min<sup>-1</sup>). DR UV-Vis spectra of the samples were recorded (200-800 nm) using Shimadzu UV-2450 spectrophotometer equipped with diffuse reflection attachment and BaSO<sub>4</sub> was used as a reference. Raman spectra were recorded using EZ-Raman 785 series, Diode Laser power 60 mW. FTIR spectra were recorded using PerkinElmer Spectrometer (FT-IR C101375). The prepared sample was mixed with KBr and compressed to form a thin pellet for FT-IR analysis.

#### Catalytic activity and reactor set-up

All the prepared Ni<sub>2</sub>P/MAS (10)-A, MoP/MAS (10)-A, MoP/MAS (10)-B, NiMoP/MAS (10)-A, and NiMoP/MAS (10)-B catalysts were screened for HDO of methyl heptanoate by tuning the various reaction parameters such as temperature (250 to 375°C), pressure (10 to 40 bar) and WHSV (1.7-  $8.5 h^{-1}$ ). The product was collected for every one hour interval and analyzed in a gas chromatograph (Shimadzu-GC-17A with DB-5 column). Prior to each run, all the catalysts were activated under nitrogen atmosphere at 400°C followed by passing ultrahigh pure hydrogen gas for 4h under 4 bar pressure.

Vapour phase HDO of methyl heptanoate was carried out in a high throughput reactor setup; Stainless steel high pressure fixed bed flow reactor (100 bar) fabricated by Amar Equipment (India) Pvt. Ltd, Mumbai, India. A schematic diagram of the high pressure fixed bed flow reactor set-up is shown in Figure S1. In this work, high purity hydrogen and nitrogen gas and methyl heptanoate dissolved in m-xylene were used as a feed. Both temperature and pressure were monitored by the pneumatic control panel. The pelletized catalyst was packed with glass beads (3.5 mm diameter) inside the bed (15 mm inner diameter and 380 mm in length) which was in turn densely packed with silica wool to maintain a uniform temperature throughout the bed. The gas feed (N<sub>2</sub>,  $H_2$ , and  $O_2$ ) along with vaporized methyl heptanoate was introduced as a single feed to the reactor tube with the aid of high pressure pump.

The % of methyl heptanoate (MH) conversion (Y) and selectivity (Si) were calculated using the following equations

Y= (mole of MH) in-(mole of MH)<sub>out</sub>/(mole of MH)<sub>in</sub> × 100% (1) S<sub>i</sub> = (mole of Product *i*)/(sum of moles all products) × 100 % (2) The specific reaction rate (SRR, r) was calculated by using the formula  $w/(Fo)=\int dXA/r=1/r\int dXA=XA/r$  (3)

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Where,  $F_o = Flow$  rate of methyl heptanoate (modeg: $\frac{1}{A} R_{e}^{-1} O H_{in} \overline{e}$ ) methyl heptanoate conversion (%) and  $W^{1\oplus 1}W^{2} R^{1} O F^{1} R^{2}$ catalyst (g).

The Turnover frequency (TOF) was calculated using the following equation

TOF (s<sup>-1</sup>) = r (mol g<sup>-1</sup> s<sup>-1</sup>) / quantity of sites ( $\mu$ mol g<sup>-1</sup>) (4) Where, the quantity of active sites is calculated from H<sub>2</sub> chemisorption ( $\mu$ mol g<sup>-1</sup>).

# **Results and discussion**

#### **XRD** analysis

In low angle XRD patterns of all synthesized materials are displayed in Figure 1A. In case of Ni<sub>2</sub>P/MAS (10) catalysts a sharp intense diffraction peak at 20 2.42° and a less prominent peak at 3.46° corresponding to the 100 and 110 reflection planes were evidently observed, indicating long-range ordered mesoporous framework with hexagonal symmetry in the synthesized MAS (10). Absence of other planes characteristic to that of MAS were not observed which may be due to the high loading of aluminium content on the silica frame work <sup>[39]</sup>. In case of monometallic MoP/MAS (10)-A and MoP/MAS (10)-B catalysts, the diffraction peak corresponding to the 100 plane of MAS was observed at 2.39° whereas in the bimetallic NiMoP/MAS (10) A and NiMoP/MAS (10) B catalysts the peak due to 100 plane of MAS was shifted to 20 value of 2.42°. The mesoporous nature of MAS was found to be retained and not distorted as evident as seen from HR-TEM images (Figure 6).

Figure 1B depicts the high angle XRD pattern of all the prepared catalysts. XRD pattern of Ni<sub>2</sub>P/MAS (10) showed a broad peak at  $2\theta$  value  $23^{\circ}$  corresponding to the amorphous nature of silica-alumina framework of MAS support. Absence of any peak characteristic to the Ni<sub>2</sub>P phase in the diffraction pattern of Ni<sub>2</sub>P/MAS (10) catalyst, implies that the phase may be well dispersed over MAS (10) support [26-27]. The XRD pattern of MoP/MAS (10) (JCPDS#24-0771) catalysts prepared under both acidic and basic medium showed a common set of peaks at 20 = 26.89°, 32.57°, 44.11°, 55.7°, 62.8°, 67.49° and 73.9° corresponding to the respective planes (001), (100), (101), (110), (111), (102) and (201) of MoP <sup>[28]</sup>. In addition, peaks characteristic to the MoO<sub>3</sub> phase were also observed at 20 = 11.1°, 30.64°, 36.05°, 39.03°, 48.32°, 51.09° and 62.88° <sup>[29]</sup>. There was no significant change observed in the peak position and peak intensity of MoP based on the medium of synthesis i.e. both MoP/MAS (10) A & MoP/MAS (10) B exhibited almost similar diffraction pattern. For bimetallic NiMoP/MAS (10) (JCPDS#30-0862) catalysts were prepared under both acidic and basic medium, a common set of, sharp crystalline peaks corresponding to the MoP phase formation over the MAS (10) support were observed. In addition to these peaks, a peak at  $2\theta = 27.5^{\circ}$ , due to the formation of crystalline Ni<sub>2</sub>P phase, was also observed for the catalyst prepared under acidic medium [30].

Catalysts on two	<sup>a</sup> S BET	<sup>b</sup> V	<sup>c</sup> d	<sup>d</sup> Reduction	<sup>d</sup> Volume of H <sub>2</sub>	eAcidity		fPhase	<sup>g</sup> Edge	
Catalysts entry	$(m^2 g^{-1})$	$(\text{cm } \text{g}^{-1})$	(nm)	(°C)	(μmol g <sup>-1</sup> )	WA	<b>SA</b>	TA	_ lormeu	(E <sub>g</sub> ) e
MAS (10)	855	0.91	9.0	-	-	-	-	-	-	-
Ni <sub>2</sub> P/MAS (10)-A	825	0.90	8.9	237,337, 377	70	0.42	0.01	0.43	$Ni_2P$	-
MoP/MAS (10)-A	662	0.79	8.5	547,726, 850	155	0.90	0.01	0.91	MoP	3.45
MoP/MAS (10)-B	640	0.77	8.3	540,675, 789	135	0.55	0.01	0.56	MoP	3.54
NiMoP/MAS(10)-A	580	0.71	8.9	449,540,675, 789	180	0.11	1.02	1.13	Ni2P, NiMoP	3.80
NiMoP/MAS(10)-B	510	0.68	8.6	552,772,850	151	0.5	0.13	0.63	Ni(OH)	3.73
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JV-VIS Spectrum, (BJH This peak was obs NiMoP/MAS (10) B c precipitation reaction conditions. thus h	) Barrett-Jo erved to atalyst, whon of Ni <sup>2</sup>	be less pr nich is due f * as Ni(Ol	rominent to the m H) <sub>2</sub> und mation	is, WA= Weak acid t in case of N ore favoured b er basic pH N of Ni3P in b	, TA = total acidity a MoP/MAS (10). Co Dimetallic catalyst values; this can be Dlockage and surfa	nd SA= S ompared s exhik e attribu ce area	trong aci I to the ited re ted to to	monom duced the grea	etallic cata pore cha ater degre ed by the	alysts, 1 racteris e of po bimeta
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## N<sub>2</sub> Sorption study

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BET isotherms and pore size distribution curves of Ni<sub>2</sub>P, MoP, and NiMoP supported MAS (10) catalysts are shown in Figure 2 (A) and (B) respectively. All the prepared catalysts displayed type-IV isotherm (H1 type hysteresis loop) with a sharp nitrogen uptake in  $P/P_0$  range of 0.5 -0.9  $P/P_0$ confirming the mesoporous nature of the catalysts <sup>[21]</sup>. In case of monometallic catalysts, Ni<sub>2</sub>P/MAS (10) exhibits greater surface area, pore volume and pore diameter as compared to

MoP/MAS (10). Compared to the monometallic catalysts, the bimetallic catalysts exhibited reduced pore characteristic values; this can be attributed to the greater degree of pore blockage and surface area coverage caused by the bimetallic species (NiMoP) as compared to their monometallic counterparts (Ni<sub>2</sub>P and MoP), on the support (Table-1)<sup>[20]</sup>. It is inferred from Table-1 that monometallic (MoP/MAS 10) and bimetallic (NiMoP/MAS 10) catalysts prepared under acidic medium showed beneficial textural properties than the one prepared under basic medium [18].



Figure 2 N<sub>2</sub>-adsorption desorption isotherms (A) and Pore size distribution curves (B) of catalysts

## DR Uv Vis spectroscopy

DR UV-vis spectra of all the catalysts are shown in Figure 3. In case of Ni<sub>2</sub>P/MAS (10) A, absorbance bands around 240–370 nm and a broad band in the range of 550–800 nm are due to the octahedral framework of Ni<sup>2+</sup> in Ni<sub>2</sub>P phase <sup>[31]</sup>. MoP/MAS (10) catalysts prepared under acidic and basic medium displayed absorbance peaks around 220, 230-285 and 285-350 nm which can be attributed to the  $\ensuremath{ T_d}$  and  $\ensuremath{O_h}$ environment of Mo respectively [20, 32]. In case of the absorbance peaks observed in common, in the range of 285-359 nm, for both acidic and basic medium synthesized MoP/MAS (10) catalyst, a shift in the absorbance peaks towards higher wavelength was noted in case of MoP/MAS (10) A, indicating greater number of O<sub>h</sub> coordinated species in

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the MoP/MAS (10) A as compared to the MoP/MAS (10) B catalyst. In case of bimetallic catalysts, NiMoP/MAS (10) all the absorbance bands corresponding to T<sub>d</sub> and O<sub>h</sub> environment of Mo were evident at 220, 230-285 and 285-350 nm respectively. A similar trend, as observed in case of monometallic MoP/MAS (10) catalysts, was more evidently observed in case of bimetallic NiMoP/MAS (10); a shift in the absorbance bands towards the higher wavelength was observed in case of NiMoP/MAS (10) A as compared to NiMoP/MAS (10) B, indicating more number of octahedrally bonded species in the NiMoP/MAS (10) A than the NiMoP/MAS (10) B catalyst. Other than the bands characteristic to the Mo species, both acidic and basic medium synthesized NiMoP/MAS (10) catalysts exhibited absorption bands at 600 and 750 nm, characteristic to the octahedral species of Ni<sup>2+</sup>.

Moreover, it is an established fact that an increase in Al content in the alumino-silicates increases the edge energy ( $E_g$ ) values in terms of the blue shift of molybdenum absorption edge as reported in literature <sup>[33]</sup>. The edge energy value for the bimetallic NiMoP/MAS (10)-A catalyst was calculated to be 3.80 eV which was found to be higher than the edge energy value of NiMoP/MAS (10)-B (3.73 eV) (Table 1); this clearly implies and once again emphasizes that a large number of octahedral coordinated molybdenum phosphate species was formed in case of NiMoP/MAS (10) A as compared to NiMoP/MAS (10) B catalyst <sup>[39]</sup>.



#### NH<sub>3</sub>-TPD analysis

Temperature programmed desorption profiles of all the catalysts are shown in Figure 4. The acid sites of the solid samples were categorized as weak (100 - 250°C), medium (250 - 450°C) and strong acid sites (above 450°C) based on the temperature programmed desorption of NH<sub>3</sub> at various temperatures <sup>[34]</sup>. Table 1 summarizes the total acidity of all the catalysts prepared under both acidic and basic medium. The NH<sub>3</sub>-TPD profiles of monometallic MoP/MAS (10) and bimetallic NiMoP/MAS (10) catalysts were greatly influenced by the medium of preparation (acidic or basic) and correspondingly exhibited strong and weak acid sites. The total acidity values of all the catalysts were measured to be in the range of 0.43 to 1.13 mmol g<sup>-1</sup>. Among all the catalysts, the

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total acidity values measured on bimetallic NiMoP/MAS (10) As was found to be the highest (1.13 mMol  $12^{-1}$ ). This was found to be the highest (1.13 mMol  $12^{-1}$ ). This was found to the creation of large amount of H<sup>+</sup> ions and H atoms on the catalyst surface by the Ni<sub>2</sub>P species <sup>[20]</sup>. The surface hydroxyl groups on the support, stabilizes these hydrogen species which in turn is responsible for high acidity value. The order of acidity follows the trend; NiMoP/MAS (10)-A > MoP/MAS (10)-A > NiMoP/MAS (10)-B > MoP/MAS (10)-B > Ni<sub>2</sub>P/MAS (10)-A catalysts.



Figure 4 NH<sub>3</sub>-Temperature Programmed Desorption profiles of catalysts

#### H<sub>2</sub>-TPR analysis

In order to ascertain the fact, that the conditions employed in the method of preparation, the metal precursors used and the type of support can alter the reduction temperature of Ni and Mo active metal species [36], H2-TPR study was carried out for all the synthesized catalysts. The H<sub>2</sub>-TPR profiles of Ni<sub>2</sub>P/MAS (10)-A, MoP/MAS (10)-A, MoP/MAS (10)-B, NiMoP/MAS (10)-A, and NiMoP/MAS (10)-B catalysts are displayed in Figure 5. The as-synthesized catalysts were subjected to TPR using H<sub>2</sub> gas. The H<sub>2</sub>-TPR profiles were recorded up to 650°C at the rate of 1°C min-1. In case of Ni<sub>2</sub>P/MAS (10) catalyst, two types of reduction peaks were displayed at 337 and 377°C corresponding to the reduction of Ni<sup>2+</sup> in the Ni<sub>2</sub>P phase. The preparation conditions employed in the formation of Ni<sub>2</sub>P phase facilitates the reduction of Ni at lower temperature (377°C) as compared to the previously reported data wherein the reduction of supported Ni<sup>2+</sup> species has been recorded at higher temperature <sup>[37]</sup>. NiMoP/MAS (10) A and B showed three types of reduction peaks at 540, 740 and 820°C corresponding to the reduction of different Mo species. Reduction peak observed at 540°C is due to the reduction of Mo6+ to Mo4+ in the form of octahedral polymolybdates, whereas reduction peak observed at 740°C is ascribed to Ni<sup>2+</sup> to Ni<sup>0</sup> in the bimetallic nature of active metals <sup>[38, 52]</sup>. Further the reduction peak at 820°C is ascribed to the reduction of tetrahedrally coordinated of Mo<sup>6+</sup> to Mo<sup>0 [38, 52]</sup>.

For the catalyst NiMoP/MAS (10)-A prepared under acidic medium, a lower temperature shoulder peak at  $449^{\circ}$ C, arising due to the reduction of the Ni<sub>2</sub>P phase was evident;

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however, such a low-temperature reduction peak was not observed in the NiMoP/MAS (10)-B catalyst. This evidently proves that the enhanced reduction capacity of NiMoP/MAS (10)-A catalyst has increased the performance of hydrotreating reaction when compared to the NiMoP/MAS (10)-B catalyst.

The hydrogen consumptions values calculated by H<sub>2</sub>-TPR profiles are tabulated in Table 1. The hydrogen consumption value of NiMoP/MAS (10)-A (180  $\mu mol~g^{\text{-1}})$  is greater than Ni<sub>2</sub>P/MAS (10) (70  $\mu$ mol g<sup>-1</sup>) catalyst. The activities of catalysts were direct by correlated with the hydrogen consumption values.



Figure 5 H<sub>2</sub>-Temperature Programmed Reduction Profiles of catalysts

#### **FT-IR Spectroscopy**

The FT-IR spectra of all the synthesized catalysts are displayed in Figure S2. The peaks pertaining to that of MAS (10) support were seen in common in case of all the synthesized catalysts. The peaks observed at 1058 and 802 cm<sup>-</sup> <sup>1</sup> can be unambiguously ascribed to the asymmetric and symmetric stretching vibrations respectively of the Si-O-Al bond in the support. The absorbance band observed at 3500 cm<sup>-1</sup> corresponds to the -OH group of the MAS (10) support <sup>[26]</sup>. The absorbance band observed at 1050 cm<sup>-1</sup> is due to the formation of P=O and P-O-Ni bond in all the prepared catalysts which is in accordance with the previously reported literature <sup>[39]</sup>. The stretching vibration mode of Ni-P bond appeared around 900-1000 cm<sup>-1</sup> and the bending mode vibration was observed at 481 cm<sup>-1</sup> in case of Ni<sub>2</sub>P/MAS (10) and NiMoP/MAS(10) <sup>[28]</sup>. The broad band at 1050 cm<sup>-1</sup> in Ni<sub>2</sub>P/MAS (10)-A catalyst is ascribed to strong asymmetric vibration of Si-O-P. The band observed at 953 cm<sup>-1</sup> is a clear indication of P-Ni bond in NiMoP/MAS (10)-A catalyst and the absorption band at 965 cm<sup>-1</sup> corresponds to Mo-O-P bond <sup>[37, 40]</sup>. The results confirm that the bands characteristic to NiP and MoP were evidently observed in the MAS (10) supported bimetallic NiMoP catalysts prepared under acidic medium. However, these characteristic bands were weak and less intense in MoP/MAS (10)-B and NiMoP/MAS (10)-B catalysts. **Raman analysis** 

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Raman spectroscopy is an important artopholin determining the structural information of the of th Raman spectra for Ni<sub>2</sub>P/MAS (10)-A, MoP/MAS (10)-A, MoP/MAS (10)-B, NiMoP/MAS (10)-A, and NiMoP/MAS (10)-B are presented in Figure S3. In case of Ni<sub>2</sub>P/MAS (10) A catalyst, two Raman bands at 855 and 416 cm<sup>-1</sup> were observed, which reveals the formation of Ni<sub>2</sub>P phase over MAS (10) support <sup>[12]</sup>. In case of MoP/MAS (10)-A catalyst, six Raman bands were observed at 121, 285, 418, 666, 817, and 990  $\mbox{cm}^{-1}$ corresponding to the crystalline MoP phase, among these the bands observed at 285, 817 and 990 cm<sup>-1</sup> can be attributed to the polymeric form of molybdate <sup>[41]</sup>. The set of Raman bands observed in case of the monometallic catalysts were sharp, indicating crystalline nature; whereas the bands were broad indicating amorphous nature in case of bimetallic catalysts. For the bimetallic catalysts, there are six Raman bands observed at 269, 427, 653, 821, 989, and 1087 cm<sup>-1</sup> that can be ascribed to the amorphous nature of NiMoP phase, among these the peaks observed at 269, 821, and 989 cm<sup>-1</sup> reveals the formation of Ni-Mo-P-O bond. As compared to monometallic MoP/MAS(10), peak at 1087 cm<sup>-1</sup> due to  $v_{as}$  (P-O) of PO<sub>4</sub> group was much more evident in the bimetallic catalyst [42] and the broad peak at 989 cm<sup>-1</sup> ascribed to  $v_{as}$  (Mo = O) of octahedral coordinated polymeric molybdate was observed both in case of monometallic MoP/MAS (10) as well as bimetallic catalyst. Other common bands observed in both monometallic MoP/MAS (10) and the bimetallic catalysts included the strong band at 817 cm<sup>-1</sup> attributed to  $v_{as}$  (Mo-O-Mo) of polymeric molybdate and another weak band at 427 cm<sup>-1</sup> ascribed to the vibrational mode of the P-O-Mo bond [39]. In comparison to all the catalysts, NiMoP catalyst synthesized under basic medium possessed the most amorphous nature which can be inferred from the broad Raman bands. Moreover, the band at 805 cm<sup>-1</sup> observed in NiMoP/MAS (10)-B catalyst, corresponds to the Ni (OH)<sub>2</sub> phase. Both, its amorphous nature and the precipitation of Ni<sup>2+</sup> as Ni (OH)<sub>2</sub> were also hinted from the XRD results of NiMoP/MAS (10)B as discussed in XRD.

#### **SEM and HR-TEM studies**

SEM images of NiMoP/MAS (10)-A catalyst is shown in Figure 6 A-B. The images of the NiMoP/MAS (10)-A catalyst seems like an encrusted surface with spherical morphology of the support. Even after deposition of NiMoP species over the MAS (10) support, the spherical morphology of the support has been retained. HR-TEM images of NiMoP/MAS (10)-A catalyst is shown in Figure 6 C-D. The catalyst showed ordered mesoporous nature of the support and the observed dark patches confirms the dispersion of NiMoP species over the support.Both SEM and HR-TEM images reveal spherical morphology, ordered porous nature and homogeneous dispersion of NiMoP/MAS species over the MAS (10) support. It must also be noted that the low pH conditions (acidic medium) deployed in the synthesis of NiMoP/MAS (10)-A catalyst, has not destructively affected the morphology of either the support or the catalytic active species; however its

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constructive benefits are evidently reflected in its catalytic activity as discussed further.



Figure 6 SEM (A & B) and HR-TEM images (C & D) of NiMoP/MAS (10)-A catalyst

# **Catalytic activity**

#### Effect of reaction temperature

The Hydrodeoxygenation activity of Ni<sub>2</sub>P/MAS (10)-A, MoP/MAS (10)-A, MoP/MAS (9)-B, NiMoP/MAS (10)-A, and NiMoP/MAS (10)-B catalysts were measured in the temperatures ranging from 250 to 375°C under 30 bar H<sub>2</sub> pressure and the results are shown in Figure 7 A. At 250 °C the conversion of methyl heptanoate over the catalysts Ni<sub>2</sub>P/MAS (10)-A, MOP/MAS (10)-A, MOP/MAS (10)-B, NIMOP/MAS (10)-A, and NiMoP/MAS (10)-B was calculated to be 50, 60, 59, 72, and 65 % respectively and further increase in the temperature up to 350 °C led to further increase in methyl heptanoate conversion. At 350 °C, the methyl heptanoate conversion over the catalysts was evaluated to be 57, 77, 76, 99, and 80 % respectively. Further increase in temperature beyond 350 °C, there was a slight decrease in the conversion which may be probably due to coke formation on the surface of the catalysts as shown in Figure 7 (A). NiMoP/MAS (10)-A catalyst prepared under acidic medium showed maximum conversion towards methyl heptanoate (>99%) as compared to NiMoP/MAS (10)-B and all the other synthesized catalysts. Hence, 350 °C was chosen as the optimum temperature for further studies.

#### Effect of reaction H<sub>2</sub> pressure

Effect The effect of pressure on hydrodeoxygenation of methyl heptanoate was studied on all the catalysts and the results are shown in Figure 7 B. Initially, the reaction was carried out at 350 °C under 10 bar H<sub>2</sub> pressure. The conversion of methyl heptanoate on Ni<sub>2</sub>P/MAS (10)-A, MoP/MAS (10)-A, MoP/MAS (10)-B, NiMoP/MAS (10)-A, and NiMoP/MAS (10)-B catalysts were calculated to be 45, 71, 60, 83 and 66.8 % respectively. Upon increasing the pressure up to 30 bar, maximum conversion was recorded for all the catalysts. On further increasing the H<sub>2</sub> pressure (40 bar), the conversion slightly decreased for all the catalysts, probably due to crowding of the reactant molecule on the catalyst surface, which results in decreased reactant contact\_time\_covecitie catalyst. Once again, NiMoP/MAS (10)-A catalyst prepared under acidic medium exhibited maximum methyl heptanoate conversion as compared to NiMoP/MAS (10)-B and all the other synthesized catalysts. Based on this observation, 30 bar H<sub>2</sub> pressure was chosen as the optimum pressure for further studies.



Figure 7 (A) Effect of reaction temperature on HDO of Methyl<br/>heptanoate at 30 bar H2 pressure, (B) Effect of reaction H2<br/>pressure on HDO of Methyl heptanoate at 350°C. (Reaction<br/>conditions; Methyl heptanoate 7 % in m-xylene, WHSV=  $3.42h^{-1}$ ,<br/>H2 flow rate = 1200 ml/h)

#### HDO activity of the catalysts

Catalyst A detailed comparison of the NiMoP/MAS (10)-A was made at 275°C and 350°C under 30 bar H<sub>2</sub> pressure with all the other catalysts in order to understand the HDO efficiency; these results are displayed in Figure S4 A & B; the SRR and TOF values are tabulated in Table 2. The possible route for upgradation of methyl heptanoate takes place either by decarboxylation to  $C_6$  alkane or HDO to  $C_7$  alkane. At 275°C, most of the reactant molecule prefers to undergo HDO to C7 hydrocarbon (50% selectivity) rather than decarboxylation to C6 hydrocarbon (20% selectivity) on the Ni<sub>2</sub>P/MAS (10) catalyst, since the Ni<sup>2+</sup> sites are associated with superior hydrogenation ability which has been evidently proved for fatty acid methyl ester (FAME) conversion on Ni<sub>2</sub>P/SBA-15 catalyst <sup>[43]</sup>. At 275°C, similar HDO pathway was followed by both MoP/MAS (10)-A & MoP/MAS (10)-B catalysts but with higher conversion (62 & 58%) and selectivity towards C7 hydrocarbon (58 and 55%) compared to Ni<sub>2</sub>P/MAS (10) catalysts. It was also observed that HDO to C<sub>7</sub> hydrocarbon is more favourable over MoP/MAS (10)-A than over MoP/MAS (10)-B catalyst. The catalytic activity not only depends on the textual properties of the catalysts but also on various parameters involved such as hydrogen consumption (H<sub>2</sub>-TPR), metal - support interaction (H<sub>2</sub>-TPR profiles), acidity (NH<sub>3</sub>-TPD), surface coverage of Mo-Ni active metals (BET analysis) and chemical environment of the catalysts (Raman and DRS-Uv-Visible).

Table 2Comparative account of catalytic activity, SpecificReaction Rate, TOF, Metal Dispersion, No of  $H_2$  active sites forHDO of methyl heptanoate on Ni<sub>2</sub>P/MAS (10)-A, MoP/MAS

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6 . I .	<sup>a</sup> H <sub>2</sub> active	<b>SRR x 10<sup>-4</sup></b> mol g <sup>-1</sup> s <sup>-1</sup>		TOF s <sup>-1</sup>		. CE	
Latalysts	<b>site</b> × 10 <sup>-6</sup> g <sup>-1</sup> )	<b>275</b> (°C)	<b>350</b> (°C)	<b>275</b> (°C)	<b>350</b> (°C)	SF	
Ni <sub>2</sub> P/MAS(10)A	20.8	3.8	4.5	1.8	2.1	-	
MoP/MAS (10)-A	12.7	4.3	5.5	3.3	4.3	-	
MoP/MAS (10)-B	11.2	4.0	5.2	3.1	4.0	-	
NiMoP/MAS (10) A	8.50	5.2	6.9	6.1	8.1	3.8	
NiMoP/MAS (10)-B	9.00	4.4	6.1	4.9	6.7	3.2	

 $^{a}H_{2}$  chemisorption Studies SF = synergetic factor, and Reaction conditions: 7% Methyl heptanoate, 30 bar H<sub>2</sub> pressure, reaction time: 5 h; catalyst pellet size 0.5-1 mm, catalysts weight 2 g, WHSV 3.4 h<sup>-1</sup>and H<sub>2</sub> flow rate = 1200 ml/h.

At 275°C temperature, both bimetallic catalysts NiMoP/MAS (10)-A and NiMoP/MAS (10)-B displayed significant improvement in conversion (75 and 64%) and selectivity to C7 hydrocarbon (70 and 60%) due to the presence of promoter Ni<sub>2</sub>P phase. In order to understand the Ni2P promotion, the synergetic factor for the bimetallic catalysts was calculated and is presented in Table (2). Large value of acidity and hydrogen spill over are responsible for the high synergetic factor of the NiMoP/MAS (10)-A as evidenced from the TPD/TPR results. The high hydrogen consumption values of pre-reduced Mo species on NiMoP/MAS (10)-A catalyst supports this positive synergism (Table 2). The H<sub>2</sub> consumption values for various catalysts are shown in Table 1. This may be attributed due to the activation and stabilization of MoP phase by the promoter phase Ni<sub>2</sub>P.

It seems to be clear that high temperature (at 350°C) favours C<sub>6</sub> hydrocarbon formation which inclines to follow the decarboxylation process rather than the HDO pathway on all the catalysts. Compared to the monometallic catalysts, extensive C<sub>6</sub> hydrocarbon formation is observed on bimetallic catalysts as shown in Figure S4 B and Table 2. Hence it is clear that, decarboxylation process becomes more favourable when both Ni<sub>2</sub>P and MoP phases coexists rather than over monometallic phases, Ni<sub>2</sub>P or MoP. Further it can be understood that HDO and decarboxylation of methyl heptanoate are dependent on both temperature and type of metallic phase. Decarboxylation and hydrodeoxygenation pathways are simultaneously taking place on all the catalysts at all the temperatures. Hence, by adjusting the reaction temperature and metallic phase, hydrodeoxygenation versus decarboxylation of methyl heptanoate can be controlled.

#### Plausible reaction path ways

The reaction pathways conceivably followed by all the catalysts are shown in Figure S5. HDO of methyl heptanoate takes place via two major routes namely hydrodeoxygenation and decarboxylation. In the first route, HDO of methyl heptanoate occurs by the formation of 1-heptanol and methanol, followed by  $E_2$  elimination to produce 1-heptene

<sup>[43]</sup>. Then hydrogenation of 1-heptene leads to  $n_{\text{blue particle}}^{\text{[43]}}$ . Then hydrogenation of 1-heptene leads to  $n_{\text{blue particle}}^{\text{[43]}}$ . Then hydrogenation of 1-heptene leads to  $n_{\text{blue particle}}^{\text{[43]}}$  methyl heptanoate takes place to form heptanoic acid and methanol followed by decarboxylation to produce  $C_6$  hydrocarbon. Among the routes, the first route was favoured at 275°C with less amount of formation of  $CO_2$  leading to the formation of  $C_7$  hydrocarbon predominantly on all the catalysts. The second route occurred at 350°C by predominant decarboxylation of methyl heptanoate to form  $C_6$  hydrocarbon. This has been reported to be the preferred reaction at high temperature <sup>[44]</sup>. The temperature of the reaction seemingly decides the pathway of the reaction under the assayed reaction conditions.

#### **Catalytic activity**

The catalytic activity of Ni<sub>2</sub>P/MAS (10)-A, MoP/MAS (10)-A, MoP/MAS (10)-B, NiMoP/MAS (10)-A, and NiMoP/MAS (10)-B catalysts were calculated at 350°C temperature under 30 bar H<sub>2</sub> pressure and the results are shown in Figure S6; specific reaction rate (SRR), TOF values, conversion and selectivity of HDO reaction towards methyl heptanoate are included in Table 2. The monometallic Ni<sub>2</sub>P/MAS (10) catalyst exhibited least conversion of about 65% and SRR and TOF values of  $4.5 \times 10^{-4}$  mol g<sup>-1</sup> s<sup>-1</sup> and 2.1 s<sup>-1</sup> respectively, which may be due to the undesirable hydrogenation ability of the monometallic NiP phase on the support. It is clear that the reactant molecule on NiP phase prefers hydrogenation instead of C-O cleavage.

The monometallic MoP/MAS (10)-A catalyst exhibited moderate conversion (80%), SRR (5.5  $\times$  10<sup>-4</sup> mol g<sup>-1</sup> s<sup>-1</sup>) and TOF (4.3 s<sup>-1</sup>) values. Among all the catalysts, NiMoP/MAS (10)-A catalyst showed maximum conversion (100 %) with  $C_6-C_7$ hydrocarbon selectivity. SRR and TOF values for the NiMoP/MAS (10)-A catalyst was calculated to be  $6.9 \times 10^{-4}$  mol g<sup>-1</sup> s<sup>-1</sup> and 8.1 s<sup>-1</sup>. The maximum HDO rate of the catalyst can be correlated with high hydrogen uptake value (180 mmol g<sup>-1</sup>), increased total acidity (1.13 mmol g<sup>-1</sup>) and fine dispersion of the active metal compounds over the support as evidenced from the NH<sub>3</sub>-TPD/H<sub>2</sub>-TPR and XRD results. Moreover, NiP phase present in the bimetallic NiMoP/MAS (10)-A catalyst potentially enhances the hydrogen spill over on the surface, which minimizes coke formation on the catalyst surface [23]. The activity of the catalysts follows the trend Ni-MoP/MAS (10)-A>Ni-MoP/MAS (10)-B>MoP/MAS (10)-A>MoP/MAS (10)-B>Ni<sub>2</sub>P/MAS (10)-A. The superior HDO activity of NiMoP/MAS (10)-A catalyst is strongly related to the acidic method of preparation and promotional sites offered by the Ni<sub>2</sub>P phase. Moreover, it is evident from Table 2 that the value of synergetic effect of the NiMoP/MAS (10)-A catalyst is more positive than NiMoP/MAS (10)-B. This directly explains why the production of spillover hydrogen is higher in the former catalyst than the latter at low temperature. Hence, the formed Ni<sub>2</sub>P phase can split the hydrogen which can be adsorbed over

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Table 3 Critical evaluation of the catalytic potency of var	rious catalysts for vapour phase HDO reaction
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S. N	Catalysts	Reactant	Conversion (%)	Reaction condition	TOF s <sup>-1</sup>	Paraffin' s	Ref
1	NiMoP/MAS	Methyl Heptanoate	100% Yield 92 wt	2% 3MPa,WHSV=3.4h <sup>-1</sup> ,	8.1	C <sub>6</sub> -C <sub>7</sub>	This
	(10)-A			350 °C			work
2	Ni <sub>2</sub> P/SAPO-11	Methyl Laurate	99 wt%	3MPa, 300-340°C	0.68	$C_{11}$ - $C_{12}$	[47]
3	$Ni_3P$ - $i_{12}P_5/Al_2O_3$	Methyl Laurate	99 wt%	3.0MPa, 300-340°C	0.28	$C_{11}$ - $C_{12}$	[47]
4	NiMo/Al <sub>2</sub> O <sub>3</sub>	Sun flower	82-90 wt%	8MPa,LHSV=1h <sup>-1</sup>	-	$C_{15}$ - $C_{20}$	[48]
				360-380°C			
5	NiW/Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	Soybean	85-95 wt%	5MPa,340-	-	$C_{15}$ - $C_{20}$	[49]
	NiMo/Al <sub>2</sub> O <sub>3</sub>			380°C,LHSV=2.4 h <sup>-1</sup>			
6	Hydrotreating	Waste	72.62%, Yie	ld: 330-398°C,	-	C <sub>8</sub> -C <sub>29</sub>	[50]
	catalyst	cooking oil	71wt%,	8.3MPa,LHSV=1 h <sup>-1</sup>			
7	NiMo/zeolite	Palm	Yield:11.93wt%	300-320 ºC,1 atm	-	$C_{15}$ - $C_{20}$	[51]

the MoP to activate the catalytic centres which are responsible for enhanced hydrogenation and effective HDO ability of NiMoP/MAS (10)-A catalyst.

Based on the available literature, a comparative study was done, in terms of the catalyst and the model compound used, reaction conditions employed, the hydrocarbon formed, the % conversion, yield and TOF for the reaction, in order to ascertain the competency of the catalyst synthesized in this work with respect to the already published work for vapour phase HDO reactions. The available data are tabulated and presented in Table 3. Fascinatingly, it was discerned that the catalyst identified in the present investigation was not only competent but also excelled the other catalysts in almost all parameters. Another striking characteristic that was brought to light is that the catalyst presented in this investigation generated the maximum yield of hydrocarbon at lower pressure as compared to the rest, which means it is a low energy consumption process. The superior activity of the synthesized catalyst originate from the combinatorial factors viz., ordered mesoporous support with high specific surface area and optimum acidity originated from the alumino silicate framework; the promotional effect of Ni<sub>2</sub>P and combination with MoP phase recorded the synergistic benefit. The optimum pH is to be maintained during the catalyst synthesis is a key parameter to tune the physicochemical characteristics of the catalyst and achieve high activity.

# Effect of WHSV and Time on Stream

Effect of WHSV was studied using the best NiMoP/MAS (10)-A catalyst for conversion and hydrocarbon selectivity of methyl heptanoate at optimized temperature (350°C) and pressure (30 bar H<sub>2</sub> pressure). The change in conversion and selectivity was investigated in the range of 1.7-8.5 h<sup>-1</sup> and results are presented in Figure 8 A. Maximum conversion and hydrocarbon selectivity (C<sub>6</sub>-C<sub>7</sub>) were measured to be 100% and 98% respectively at 3.4 h<sup>-1</sup>. Beyond the space velocity a 3.4 h<sup>-1</sup>, the conversion and selectivity decreased due to less residence time of the reactant molecules over the

surface of the catalyst which results in the reactant molecules being detached from the catalysts bed as unreacted molecules. Hence, this study confirms the optimum WHSV to be  $3.4 h^{-1}$  for maximum conversion and selectivity under optimized reaction conditions.



Figure 8 (A) Effect of WHSV on HDO of methyl heptanoate and<br/>(B) Time on stream for HDO of methyl heptanoate at  $350^{\circ}$ C<br/>under 30 bar  $H_2$  pressure.

Effect of time-on-stream was evaluated up to 15 h on highly active NiMoP/MAS (10)-A catalyst for conversion and  $C_6-C_7$  hydrocarbon selectivity of methyl heptanoate at optimized temperature (350°C) and pressure (30 bar) and the results are displayed in Figure 8 B. After 1 h, it was observed that 60% of methyl heptanoate was converted with 78% selectivity of  $C_6-C_7$  hydrocarbon. The conversion and HDO activity of the catalyst increased with increase in time and reached maximum activity at 5h, beyond which it remained constant. The  $C_6-C_7$  hydrocarbon selectivity of the catalyst was calculated to be 99%. It is obvious that the steady state condition has been maintained after 5h in the 15h experiment. The experiment could not be carried out beyond 15h due to the limitation of the reactor capacity volume.

It is reusable. The used catalyst can be regenerated by heating at 400°C for 6h under inert atmosphere to remove the surface adsorbed carbon residue and followed by reduction with high pure hydrogen to from the active metal species for the HDO reaction.

# pH role in catalysts

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In this work, pH plays a vital role in which it can alter the properties of the catalysts. Catalysts are prepared in both acidic and basic medium by altering the pH. By altering pH, intrinsic and extrinsic properties of catalyst such as surface composition, surface acidity, reducibility, chemisorption, surface coordination and surface morphology are significantly modified. In this investigation, the catalyst were prepared using active metals like nickel, molybdenum and phosphate with the ratios of Ni/P = 0.3, Mo/P = 0.06 and Ni/Mo = 0.2 by impregnation method. These catalysts were examined by different physico-chemical characterization techniques and the results revealed that at low pH (acidic medium), nickel species are highly dispersed over support and form Ni<sub>2</sub>P species in Ni-MoP/MAS (10) catalysts. (H<sub>2</sub>-TPR profile (Table 1)). Nickel act as a promoter by hydrogen spillover effect, which play an important role in HDO activity. In the catalysts synthesized under acidic medium, the H<sub>2</sub>-TPR and DR UV-Vis spectra indicated there is a strong metal support interaction (Figure 3 & 5 and Table 1). However, at high pH (basic medium), nickel species tend to precipitate as nickel hydroxide Ni (OH)<sub>2</sub>, thereby showing low the HDO activity.

#### **Mass Transfer Considerations**

Major steps involved in the catalytic reaction system are (a) diffusion of hydrogen gas feed into the liquid feed (b) adsorption of reactant from the bulk feed onto the catalyst surface (c) chemical reaction at the active sites of the catalyst (d) product desorption and diffusion from the catalyst surface. The slowest step determines the overall rate of the reaction. In order to rule out mass transfer limitations in a catalytic process, a deeper investigation has to be done to prove that the diffusion controlled steps do not alter the kinetics of the reaction. The rate of a reaction is projected from the TOF values. Thus in order to prove that both internal as well as external resistance to mass transfer are absent, two sets of experiments were carried out, based on the reports published by Ancheyta et al. <sup>[45]</sup>.

In the first set of experiments the temperature (350°C), pressure (30 bar) and WHSV (3.4 h<sup>-1</sup>) parameters were kept constant. However, the feed flow rate and the amount of catalyst were varied from 0.113 to 0.227 ml min<sup>-1</sup> and 2 to 4 g, respectively. The corresponding results have been tabulated in Table S1. Comprehension of these results show that, despite changes in the flow rate of the feed no significant change was observed in the TOF values, which proves that external mass transfer resistance was absent <sup>[46]</sup>.

In another set of experiments, to show that the kinetics of the reaction is not affected by the internal mass transfer resistance, temperature ( $350^{\circ}$ C), pressure (30 bar), feed flow rate, catalyst amount (2g) and WHSV ( $3.4 h^{-1}$ ) were kept constants. The catalysts were finely powdered and packed into two different pellet sizes (0.5-1 mm and 3-4 mm). The corresponding results have been included in Table S1,

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which once again showed no change in the TOF values, despite the changes made in the size of the Catalyst the changes made in the size of the Catalyst the NUTFISTS apparently due to the absence of mass transfer resistance. Thus since the kinetics of the reaction is not altered by the variables, it can be unequivocally confirmed that the catalytic process carried out, does not suffer from any mass transfer limitations.

# Conclusion

The significant features of the report include; one pot room temperature synthesis of thermally stable, high surface area mesoporous Alumino-Silicate (Si/Al=10) which served as an excellent support facilitating homogeneous dispersion of the active metal species (Ni<sub>2</sub>P, MoP and NiMoP) and retaining its superior pore characteristic properties even after metal dispersion both on the external surface and inside of the mesoporous framework. Comprehensive evaluation of the physicochemical characterization results of all the synthesized catalysts showcase superior properties for NiMoP/MAS (10)-A such as homogeneous dispersion (TEM), pre-reducibility (H<sub>2</sub>-TPR), high hydrogen consumption (H<sub>2</sub>-TPR, 180 mmol/g) and enhanced surface acidity (NH<sub>3</sub>-TPD, 1.13 mmol/g), which evidently justifies the intrinsic role of pH in altering the physicochemical properties of the synthesized materials. Among all the catalysts tested for vapour phase hydrotreating of methyl heptanoate, NiMoP/MAS (10)-A has been the most active catalyst yielding the C<sub>7</sub> hydrocarbon predominantly through the HDO pathway, with a selectivity and conversion of 66 and 62% respectively at a low temperature of 275°C which demonstrates the high oxygen removal efficiency of the NiMoP/MAS (10)-A catalyst at 275°C with high synergism. Both internal as well as external mass transfer resistance was unequivocally ascertained. Thus NiMoP/MAS (10)-A has been suggested as a commendable catalyst for green fuel production from non-edible oils through hydrodeoxygenation under the experimental conditions.

## Acknowledgments

The authors are grateful for the financial support provided by Defence Research and Development Organisation (DRDO), New Delhi, the project sanction no. EPIR/ER/1203047/M/01/1535, dt. 16. 05. 2014. We are thankful to DRDO, University Grants Commission (UGC), and Department of Science and Technology for providing adequate instrumentation facility in the Department of Chemistry, Anna University, Chennai, Tamil Nadu, India.

# **Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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