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Kinetics of hydrodeoxygenation of stearic acid using supported nickel catalysts: Effects of supports



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ABSTRACT

The hydrodeoxygenation of fatty acids derived from vegetable and microalgal oils is a novel process for production of liquid hydrocarbon fuels well-suited with existing internal combustion engines. The hydrodeoxygenation of stearic acid was investigated in a high pressure batch reactor using n-dodecane as solvent over nickel metal catalysts supported on SiO₂, γ -Al₂O₃, and HZSM-5 in the temperature range of 533-563 K. Several supported nickel oxide catalysts with nickel loading up to 25 wt.% were prepared by incipient wetness impregnation method and reduced using hydrogen. The catalysts were then characterized by BET, TPR, H₂ pulse chemisorption, TPD, XRD, and ICP-AES. Characterization studies revealed that only dispersed nickel oxide was present up to 15 wt.% nickel loading on γ -Al₂O₃. The acidity of the supports depends on nickel loading of oxidized catalysts and increases with increasing nickel loading up to 15 wt.%. n-Pentadecane, n-hexadecane, n-heptadecane, n-octadecane, and l-octadecanol were identified as products of hydrodeoxygenation of stearic acid with n-heptadecane being primary product. The catalytic activity and selectivity to products for hydrodeoxygenation of stearic acid depends strongly on acidity of the supports. The maximum selectivity to n-heptadecane was observed with nickel supported γ -Al₂O₃ catalyst. A suitable reaction mechanism of hydrodeoxygenation of stearic acid was delineated based on products distribution. The conversion of stearic acid was increased with increasing reaction time, nickel loading on γ -Al₂O₃, temperature, and catalyst loading. Complete conversion of stearic acid was accomplished with more than 80% selectivity to n-heptadecane at reasonable reaction temperature of 563 K after 240 min of reaction using 15 wt.% Ni/γ-Al₂O₃ catalyst. An empirical kinetic model was also developed to correlate the experimental data.

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1. Introduction

The fossil fuels in the form of petroleum, coal, and natural gas are foremost sources at present to meet societal necessities of transportation fuels of the world. According to estimates of U.S. Energy Information Administration, Annual Energy Outlook 2012, the transportation segment alone consumes 27.09 quadrillion Btu in the year of 2011 which is about 28% of total energy consumption of the world (97.70 quadrillion Btu) [1]. The growing demand of transportation fuels is principally due to increasing world's population and improvements in standard of living. The incessant and large scale usages of fossil fuels are also responsible for climate change and global warming due to anthropogenic emission of carbon dioxide into earth atmosphere. Therefore, there is growing societal need of sustainable and carbon neutral sources of energy and transportation fuels to reduce enslavement on limited fossil fuels and preserve cleanliness of environment. The development of cost effective technologies for exploration of renewable

energies such as solar, wind, hydroelectricity, and biomass have thus been stimulated all over the biosphere. However, with exception of biomass, these renewable sources can merely bring solution to energy (in the form of heat and electricity) crisis of the globe somewhat. Additionally about 90% of the chemicals requirements of the planet are fulfilled from fossil fuels in general, more specifically, from naphtha and natural gas [2]. The only renewable source, biomass, being origin of fossil fuels, has enormous prospective to fulfill demand of heat, electricity, liquid transportation fuels, and chemicals of the globe. The utilization of biomass has therefore been gaining immense importance as renewable source of energies, transportation fuels, and chemicals.

Numerous technological advancements have been made in the past to manufacture liquid transportation fuels from biomass commonly known as biofuels. The gasification followed by Fischer-Tropsch synthesis (F-TS) is one of such kind of technology for transformation of biomass into synthetic liquid fuels [3]. The technology of air gasification of biomass, however, suffers from disadvantages of low hydrogen contents (8–14 vol.%) of the resultant synthesis gas [4]. The resulting synthesis gas is therefore inappropriate for production of liquid fuels and chemicals by F-TS. Although biomass gasification by oxygen has potential to produce

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Nomeno	Nomenclature							
HDO	hydrodeoxygenation							
HEPD	n-heptadecane							
HEXD	n-hexadecane							
NiAl	$Ni/\gamma - Al_2O_3$							
OCTD	n-octadecane							
OCTDL	l-octadecanol							
PEND	n-pentadecane							
SA	stearic acid							
5NiAl	$5 \text{ wt.\% Ni}/\gamma$ -Al ₂ O ₃							
10NiAl	$10 \text{ wt.\% Ni}/\gamma - \text{Al}_2\text{O}_3$							
15NiAl	$15 \text{ wt.\% Ni}/\gamma - \text{Al}_2\text{O}_3$							
25NiAl	$25 \text{ wt.\% Ni}/\gamma - \text{Al}_2\text{O}_3$							
10NiSi	10 wt.% Ni/SiO ₂							
10NiZSN	/ 10 wt.% Ni/HZSM-5							

synthesis gas with enhanced hydrogen content; economics however favors use of hydrocarbons and inexpensive coal. The fast pyrolysis is another propitious technology for thermal disintegration of biomass in absence of oxygen or in presence of significantly less oxygen required for complete combustion in the temperature range of 623-773 K to produce liquid products normally known as bio-oil. The bio-oils is however incompatible for direct use as fuel because of its high oxygen content (low calorific value) and viscosity, immiscibility with petroleum derived fuels, partial phase separation, and long term storage instability. The bio-ethanol [5,6] and bio-butanol [7,8] produced by microbial fermentation of sugars derived from sugarcane, sugar beet, and corn or lignocellulosic biomass and biodiesel [9] manufactured by transesterification of triglycerides with methanol using NaOH as catalyst are other promising bio-fuels. However, properties of these oxygenated biofuels especially bio-ethanol and bio-diesel allows for blending with petroleum derived fuels to limited extent only. Therefore, there is a strong need to pursue alternative hydrocarbon analogous bio-fuels fully compatible with present internal combustion engines.

The triglycerides (vegetable oils, animal fats, waste cooking oils, and microalgal oils) are promising renewable feedstock for production of hydrocarbon fuels because of its low functionality and oxygen content compared to cellulosic biomass. Moreover, the triglycerides are composed of linear C₈-C₂₄ fatty acids with majority of C₁₆ and C₁₈ fatty acids [10]. Therefore, removal of oxygen heteroatoms from triglycerides provides hydrocarbon fuels resembling petroleum derived fuels in the range of gasoline, diesel, and jet fuels generally known as green-gasoline, green-diesel, and green-jet fuels respectively. Significant research efforts have thus been devoted in the past on thermal and catalytic cracking of triglycerides to produce hydrocarbon fuels [11]. However, thermal and catalytic cracking of triglycerides suffers from drawback of low yield of liquid fuels and huge loss of carbon in the form of gaseous products. The hydrodeoxygenation (HDO), similar to existing hydrotreatment technology of petroleum refinery, is another promising technology for elimination of oxygen heteroatoms from triglycerides and fatty acids in the form of water to produce liquid hydrocarbon fuels with high yield. The possibility of co-processing and use of existing petroleum refinery infrastructures are additional advantages of this technology. Recognizing importance, the present work was commenced on HDO of stearic acid (SA) as model compound. The triglycerides are commercially hydrolyzed to corresponding fatty acids and glycerol either in absence of any catalysts (at 483 K and high pressure) or in presence of small amounts of sulfuric acid or, more usually, zinc oxide (423 K) [12]. Following hydrolysis, the fatty acids mixture separated by distillation could be used as feedstock for production of green-diesel [13].

Extensive works have been published in the past on deoxygenation of several variety of fatty acids such as dodecanoic acid [14], oleic acid [15,16], linoleic acid [14,16,17], lauric acid [18], SA [16,19], C₁₇-C₂₀ and C₂₂ fatty acids [20]. Several research articles have also been published on deoxygenation of esters of various fatty acids such as methyl octanoate [21], methyl and ethyl heptanoate [22,23], methyl heptanoate [24,25], methyl hexanoate, and methyl heptanoate [24]. Various metals (Pd, Ni, Ru, Pt, Ir, Os, Mo, Co, Cu, and Rh) supported on carbon and numerous metal oxides (CaO-MgO, MgO-Al₂O₃, ZrO₂-CeO₂, Al₂O₃, ZrO₂, CeO₂, SiO₂, carbon, and SBA-15) were employed as catalyst for deoxygenation of fatty acids and their esters [17–19,26–28]. The Pd/C catalysts displayed very good catalytic activity for deoxygenation of fatty acids and their esters [26].

However, only a few studies were reported on deoxygenation of SA. Snare et al. first reported catalyst/support screening for deoxygenation of SA at 573 K and 6 bars of He pressure in a semi-batch reactor and Pd/C was reported to be the best catalyst [26]. Lestari et al. reported deoxygenation of SA over palladium catalysts supported on nanocomposite carbon Sibunit in a semi-batch reactor in the temperature range of 543-573 K using 17 bars of helium pressure and n-heptadecane (HEPD) and n-pentadecane (PEND) were reported as products [29]. Lestari et al. latter extended the work using palladium nanoparticles anchored in SBA-15 as catalyst in dodecane solvent at 573 K and 17 bars of 5 vol.% H₂ in argon pressure in a semi-batch reactor [19]. HEPD and trace amounts of isomers of n-heptadecenes were reported as products. Simakova et al. studied deoxygenation of mixture of palmitic and SA (59 mol% palmitic and 40 mol% SA) in presence of palladium supported on synthetic carbon (Sibunit) in the temperature range of 533-573 K at 17.5 bars of 5 vol.% hydrogen in helium pressure in a semi-batch reactor using n-dodecane as solvent and HEPD and PEND were reported as products [30]. Ping et al. reported catalytic decarboxylation of SA over palladium nanoparticles supported on ultra-porous silica mesocellular foam at 573K under nitrogen atmosphere in batch reactor [31]. Immer et al. reported liquid phase deoxygenation of SA using 5 wt.% Pd/C catalysts using on-line quadrupole mass spectrometry under He or 10% H₂ [16]. Berenblyum et al. reported catalytic conversion of SA over palladium supported on alumina at 623 K and 6-14 bars of hydrogen pressure in a stirred autoclave [32]. HEPD was reported as main product with diheptadecylketone as by-product. It was reported that conversion of SA remained almost unaffected beyond 8 bars of hydrogen pressure.

It is evident from above discussion that HDO of fatty acids and vegetables oils have been carried out over expensive and less abundance novel metal catalysts. Extremely high cost and insufficient abundance of noble metals catalysts are one of the serious constraints for probable large scale applications. Thus development of relatively active and inexpensive metal catalysts such as nickel is desirable for HDO applications. The performance of Ni/ γ -Al₂O₃ catalysts of varying nickel loading was therefore investigated in the present work for HDO of SA. In order to understand the effects of support and acidity of the catalysts, nickel catalysts supported on silica (SiO₂) and zeolite (ZSM-5) were also prepared and tested for HDO of SA. Moreover, detailed reaction mechanism of HDO of SA was proposed based on products distribution observed for different catalysts. An empirical kinetic model was developed based on proposed mechanism to correlate experimental data.

2. Experimental

2.1. Chemicals

Nickel (II) nitrate hexahydrate $[Ni(NO_3)_2 \cdot 6H_2O, \text{ extra pure,} \ge 97\%]$, SA (SG, $\ge 97\%$), and carbon tetrachloride (purity 99.8%) were

obtained from Merck Specialties Pvt. Limited. γ -Al₂O₃ pellets (1/8" pellets, purity 99.9%) and n-dodecane (anhydrous, purity \geq 99%) were purchased from Alfa Aesar and Sigma-Aldrich respectively. All chemicals were used without further purification. SiO₂ (AEROSIL-200) and HZSM-5 (CBV 8014 with SiO₂/Al₂O₃ mole ratio of 80) were obtained from Nippon Aerosil Co. Ltd. and Zeolyst International respectively.

2.2. Catalyst preparation

The nickel supported on γ -Al₂O₃, SiO₂, and HZSM-5 catalysts were prepared by incipient wetness impregnation method using nickel (II) nitrate hexahydrate as precursor. Measured quantities of nickel precursor equivalent to desired nickel loading was first dissolved in distilled water of volume equal to or slightly excess of total pore volume of the respective supports. Prerequisite amount of powdered support was then added to the precursor solution and agitated continuously for two hrs to ensure proper mixing. The wet materials were subsequently dried overnight at 373 K followed by calcination at 823 K using air for about 6 h. The prepared γ -Al₂O₃ supported nickel oxide catalysts were reduced in a tubular furnace at 973 K under the flow of hydrogen and nickel oxide supported on SiO₂ and HZSM-5 catalysts were reduced at 723 K. The reduction temperatures of the oxidized catalysts were selected based on TPR results as discussed in subsequent section. The nickel metal supported on γ -Al₂O₃ catalysts with nickel loading of 0, 5, 10, 15, and 25 wt.% prepared in the present work were labeled as Al, 5NiAl, 10NiAl, 15NiAl, and 25NiAl respectively. 10 wt.% nickel supported on SiO₂ and HZSM-5 catalysts were designated as 10NiSi and 10NiZSM respectively throughout the article.

2.3. Catalyst characterization

Specific surface area of the prepared catalysts were determined from nitrogen adsorption/desorption isotherms data collected at 77 K in Micromeritics ASAP 2020 physisorption analyzer. The samples were first degassed under 10^{-5} torr vacuum for 6 h at 523 K to remove impurities and physically adsorbed gases, if any. The Brunauer-Emmett-Teller (BET) surface area was then determined from adsorption isotherm data in the relative pressure (*P*/*P*₀) range from 0.05 to 0.3. The pore volume was considered as volume of liquid nitrogen adsorbed at *P*/*P*₀ = 1.0 ca.

Temperature programmed reduction (TPR) studies were carried out in Micrometrics AutoChem II 2920 chemisorption analyzer. Measured amount of oxidized catalysts were loaded in U shaped quartz tube sandwiched between two layers of quartz wool. The samples were first degassed under flow of argon (30 mL/min) at 473 K for 3 h to remove adsorbed moisture and other impurities that may be present. The samples were then cooled down to 323 Kand $10 \text{ vol.}\% \text{ H}_2$ in argon gas mixture was introduced at a flow rate of 30 mL/min. The samples were heated up to 1073 K with heating rate of 10 K/min. The hydrogen consumption was monitored using a thermal conductivity detector (TCD). Pulse calibration studies were performed for quantification of hydrogen consumption.

 H_2 pulse chemisorption studies were carried out in chemisorption analyzer (AutoChem II 2920) to determine metal dispersion and active metal surface area. Measured amount of catalysts were loaded in a quartz tube and reduced at 923 K under the flow of 10 vol.% H_2 in Ar (30 mL/min) for 2 h. The gas flow was then switched over to pure He (30 mL/min) and samples were cooled down to 323 K. The He flow was continued for another half an hr to remove traces of hydrogen from the catalyst and entire flow path. Several pulses of measured quantity of 10 vol.% H_2 in Ar were then introduced till three consecutive H_2 peaks were similar. The metal dispersion and metal surface area were calculated based on amount of hydrogen chemisorbed. Powder X-ray Diffraction (XRD) patterns of the catalysts were recorded in the 2θ range of 10 to 90° in a Phillips X-ray diffractometer (X-PERT Pro PAN analytical) using CuK_{α} radiation (λ = 1.5418 Å) at 15 kV, 30 mA current, and scanning rate of 1°/min.

Temperature programmed desorption of ammonia (NH₃-TPD) were performed for quantitative determination of acidity of the prepared catalysts using Micromeritics AutoChem II 2920 chemisorption analyzer. The samples were first degassed at 473 K under He flow to remove impurities present in it. After completion of pretreatment, the samples were exposed to 10 vol.% NH₃-He mixture for an hour at 323 K and gas flow was then switched over to pure He and He flow was continued for another 1 h. Then the sample was heated up to 1273 K with heating rate of 10 K/min. The desorbed NH₃ was monitored quantitatively using TCD. The pulse calibration studies were performed for quantification of desorbed NH₃.

The elemental composition of the reduced supported nickel catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Leeman Labs Inc, USA (Model: PS 3000 UV) ICP-AES analyzer.

2.4. Experimental setup and procedure

Catalytic HDO of SA was executed in a 400 mL high pressure stainless steel batch reactor (Amar Equipments Pvt. Ltd.) equipped with a four bladed paddle type impeller with provision of stirring speed regulation. The electrically heated furnace was used to heat the reactor whose temperature was controlled within ± 1 K by a temperature controller. In a typical HDO experiment, measured amounts of SA dissolved in known volume of solvent, n-dodecane were charged into the reactor containing known quantity of catalyst. The reactor was then pressurized to 8 bars by introducing H₂ gas through high pressure gas injection port. The reactor was then started by setting desired reaction temperature and stirring speed. Final reactor pressure of about 13, 13.5, 14.0, and 14.5 bars was observed at reaction temperature of 533, 543, 553, and 563 K respectively. Constant stirring speed of 1200 rpm was maintained throughout experiments to ensure proper mixing of reaction mixture and catalysts. The first sample was collected through liquid sampling valve after reaching the desired reaction temperature. All calculations were done considering it as initial sample. Additional samples were collected at regular interval of time.

2.5. Product analysis

The liquid samples diluted with carbon tetrachloride were first centrifuged and then analyzed using a gas chromatograph (Shimadzu, GC-2014) equipped with capillary column (ZB-5HT, 60 $m \times 0.32 \text{ mm} \times 0.10 \,\mu\text{m}$) connected to flame ionization detector using nitrogen as carrier gas. The column temperature was programmed with an initial temperature of 393 K for 5 min, increased at a rate of 45 K/min to 498 K and held at this temperature for 2 min, and again increased at a rate of 20 K/min to 508 K and stayed there for 2 min. The injector and detector temperature were maintained at 613 K and 653 K respectively. The calibration of SA was performed using n-dodecane as internal standard. The products were identified using GC-MS (GCMS-QP2010 Ultra). Gas samples were analyzed using gas chromatograph equipped with packed column (Chromatopak-Carboseive-S2, 1/8" and 3 m length) connected to TCD and argon as carrier gas. The column temperature was programmed with an initial temperature of 373 K for 15 min, increased at a rate of 30 K/min to 473 K and held there for 7 min. The injector and detector temperatures were maintained at 378 K and 523 K respectively.

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Catalysts	Nickel (wt.%)	Surface area	u (m²/g)	Pore volume (cm ³ /g)		H ₂ pulse chemisorptions						
		Oxi	Red	Oxi	Red	MD	Sm					
γ-Al ₂ O ₃	-	240		0.83		-	-					
5NiAl	3.7	224	227	0.75	0.77	1.54	10.24					
10NiAl	8.1	213	201	0.72	0.67	1.73	11.50					
15NiAl	14.5	202	190	0.63	0.64	1.16	7.71					
25NiAl	23.6	168	156	0.54	0.51	1.01	6.7					
SiO ₂	-	208		-		-	-					
10NiSi	10.4	181	191	1.19	1.38	0.51	3.38					
HZSM-5	_	402		0.28		-	-					
10NiZSM	10.2	331	353	0.23	0.25	0 79	5.28					

 Table 1

 Nickel content, BET surface areas, and H₂ pulse chemisorption results of the prepared catalysts

oxi = oxidized; red = reduced; MD = metal dispersion, %; S_m = metallic surface area, m^2/g metal.

3. Results and discussion

The HDO of SA were investigated in a high pressure batch reactor using n-dodecane as solvent in presence of nickel supported γ -Al₂O₃, SiO₂, and HZSM-5 catalysts in the wide range of catalyst loadings (0.10–0.75 (w/v)%), concentrations of SA (0.11–0.18 kmol/m³), and temperatures (533–563 K). n-HEPD was identified as primary product of HDO of SA. The formation of insignificant quantity of PEND, n-hexadecane (HEXD), n-octadecane (OCTD), and l-octadecanol (OCTDL) were also observed during the reaction. The products distribution represented in terms of 'selectivity' to products used throughout the article was calculated based on weight percent of the products formed during HDO of SA.

3.1. Characterization of the catalysts

The BET surface area of pure γ -Al₂O₃, SiO₂, and HZSM-5 and nickel supported γ -Al₂O₃, SiO₂, and HZSM-5 catalysts (both oxidized and reduced) are shown in Table 1. The surface areas of 240, 208, and 402 m²/g were observed for γ -Al₂O₃, SiO₂, and HZSM-5 respectively. As observed from the table, the surface areas of both oxidized and reduced nickel supported catalysts were somewhat lesser than pure supports as expected. With increasing nickel loadings on γ -Al₂O₃, the surface area was decreased for both oxidized and reduced catalysts. The decrease of surface area with increasing nickel loading may be due to coverage of surfaces of γ -Al₂O₃ and blockage of pores by nickel or nickel oxide. The surface area of reduced NiAl catalysts was slightly lesser than that of oxidized catalysts as observed from Table 1. This may be due to sintering of nickel particles during reduction at elevated temperature (973 K). The 25NiAl exhibited lowest surface area of 168 and $156 \text{ m}^2/\text{g}$ for oxidized and reduced catalyst respectively. The oxidized 10NiSi and 10NiZSM catalysts were reduced at relatively lesser temperature (723 K) compared to NiAl catalysts. Hence reduced 10NiSi and 10NiZSM catalysts showed slightly higher surface areas compared to corresponding oxidized catalysts due to elimination of oxygen atoms from active sites and hence decrease of overall weight of the catalyst (Table 1).

The pore volume of both oxidized and reduced catalysts were decreased marginally with increasing nickel loading further indicating coverage of surface and blockage of pores by nickel or nickel oxide. The highest metal dispersion of 1.73% was observed for 10NiAl (Table 1). The lesser metal dispersion for 10NiSi and 10NiZSM compared to 10NiAl may be due to poor metal-support interaction of nickel metal with SiO₂ or HZSM-5. The nickel content of the reduced catalysts was determined by ICP-AES elemental analyzer and results obtained are presented in Table 1.

The powder XRD patterns of both oxidized and reduced supported nickel catalysts are shown in Fig. 1A and B, respectively. The powder XRD patterns of pure nickel oxide and γ -Al₂O₃ are also

shown in Fig. 1A as reference. The characteristic peaks of nickel oxide were observed at 37.3°, 43.3°, and 63°. For oxidized 5NiAl, 10NiAl, and 15NiAl catalysts, only features due to supports were observed suggesting that nickel oxide remains as dispersed phase or nickel oxide crystallite size may be too small to be detected by



Fig. 1. Powder XRD patterns of (A) nickel oxide supported on γ -Al₂O₃, HZSM-5, SiO₂, bulk NiO, γ -Al₂O₃, and HZSM-5 and (B) nickel supported on γ -Al₂O₃, SiO₂, and HZSM-5.



Fig. 2. TPR profiles of (A) 5NiAl, 10NiAl, 15NiAl, and 25NiAl and (B) 10NiSi and 10NiZSM.

XRD. A similar feature was observed for the corresponding reduced catalysts. For both oxidized and reduced 25NiAl, 10NiZSM, and 10NiSi catalysts, typical peaks corresponding to nickel oxide or nickel were observed suggesting that catalysts are associated with both dispersed and bulk nickel oxide or nickel. However, no reduction peak corresponding to bulk nickel oxide was observed in TPR profile of oxidized 10NiZSM and 10NiSi catalysts as discussed later. It may be due to presence of low concentration of bulk nickel oxide in the catalysts.

The TPR studies were performed to apprehend reducibility and to determine reduction temperatures of supported nickel oxide catalysts as shown in Fig. 2. The temperature corresponding to maximum hydrogen consumption is represented as T_{max} . Three reduction peaks corresponding to T_{max} of ~650 K, 740 K, and 950 K were observed for γ -Al₂O₃ supported nickel oxide catalysts. The lower

temperature reduction peak appeared as a shoulder was attributed to reduction of bulk nickel oxide species with less interaction with the supports. As discussed above, XRD pattern of oxidized 25NiAl catalyst also confirmed the presence of bulk nickel oxide. The moderately higher temperature reduction peak may be due to reduction of dispersed nickel oxide on γ -Al₂O₃ support. The reduction peak appeared at ~950K may be due to reduction of nickel aluminate (NiAl₂O₄). Chiuping et al. also reported formation of NiAl₂O₄ species at about 1063 K [33]. For nickel oxide supported on SiO₂ and HZSM-5 catalysts, maximum hydrogen consumption was observed at about 633 K. However, peak corresponding to reduction of bulk nickel oxide was not observed for these catalysts though their XRD patterns confirmed presence of bulk nickel oxide. This may be due to low concentration of bulk nickel oxide and/or overlap of reduction temperature of bulk nickel oxide with dispersed one. These results suggest that formation of different surface species depends on both nickel loading and types of supports. At relatively lesser nickel loading, the catalysts are associated with only dispersed nickel oxide; whereas for higher nickel loadings, bulk nickel oxides are also present in addition to dispersed nickel oxide.

3.2. Reaction mechanism

A typical chromatogram of reaction mixture (diluted with carbon tetrachloride) displaying peaks of solvent, unreacted reactant, and products of HDO of SA is shown in Fig. 3. The formation of five different products, PEND, HEXD, HEPD, OCTD, and OCTDL, were observed during HDO of SA in presence of supported nickel catalysts with HEPD being major product. The review of reaction mechanism of HDO of SA, oleic acid, and linoleic acid also revealed the formation of HEPD and isomers of HEPD as major products [15,16,29,31,32,34,35]. The SA may convert to HEPD directly following either decarboxylation or decarbonylation routes (Scheme 1). The SA undergoes decarboxylation with elimination of one mole of CO₂ resulting in the formation of HEPD. The SA may also undertake decarbonylation route with removal of one mole of CO and water each leading to formation of l-heptadecene. The lheptadecene is subsequently hydrogenated to HEPD. The metallic sites of the catalyst are responsible for both decarboxylation and decarbonylation reactions.

The catalytic reduction of SA by hydrogen is most likely to occur in presence of supported nickel metal catalysts that leads to formation of OCTDL. The OCTDL formed by catalytic reduction of SA undergoes further chemical transformation following different pathways (Scheme 1). In the first pathway, OCTDL undertakes dehydrogenation to form corresponding aldehyde which further undergoes decarbonylation reaction with elimination of one mole of CO to form HEPD [36]. The hydrogenation, dehydrogenation, and decarbonylation reactions are likely to occur on metallic sites of the catalysts. However, l-octadecanal was not detected during HDO of SA. It might be due to the fact that decarbonylation of loctadecanal is faster than dehydrogenation of OCTDL. In the second pathway, OCTDL undergoes dehydration to l-octadecene which is subsequently hydrogenated to OCTD [22]. However, 1-octadecene was not detected during HDO of SA. It may be concluded that dehydration of OCTDL is slowest and hence rate determining step. The dehydration reaction is expected to happen on acidic sites of the supports. The above statements are supported by the fact that selectivity to OCTD was increased with increasing acidity of the catalysts as discussed later. The exact mechanism of formation of PEND and HEXD during HDO of SA is however not fully clear to us. The formations of PEND and HEXD were speculated from the reaction intermediate, OCTDL.

The general consensus is that selectively diverting the reaction from reduction of fatty acids pathway to decarboxylation/decarbonylation pathway is beneficial to reduce



Fig. 3. Typical chromatogram of reaction mixture of hydrodeoxygenation of stearic acid. Conditions: concentration of SA = 0.18 kmol/m³, n-dodecane = 100 ml, catalyst loading = 0.50 (w/v)% 15NiAl, temperature = 543 K, initial hydrogen pressure = 8 bars, reaction time = 360 min.



Scheme 1. Reaction mechanism of hydrodeoxygenation of stearic acid.

Table 2						
Acidity of	of the nure	supports a	nd sun	norted r	nickel (ratalysts

Materials	Acidity (mmol NH ₃ /g)	
γ -Al ₂ O ₃	Nil	
SiO ₂	Nil	
HZSM-5	0.55	
10NiZSM	0.6	
10NiSi	0.01	
5NiAl	0.24	
10NiAl	0.26	
15NiAl	0.30	
25NiAl	0.18	

consumption of expensive hydrogen. To explore the possibility of reaction through decarxylation/decarbonylation pathway only, study was extended under nitrogen pressure over 15NiAl catalysts. No significant reaction was observed under high pressure of inert gas even at relatively higher temperature of about 623 K. This result clearly demonstrates that HDO of SA over NiAl catalysts mainly proceeds through reduction routes under the experimental conditions.

Only methane was identified as gaseous product during analysis of gaseous products. From this result it may be concluded that CO formed during HDO of SA undergo methanation reactions leading to formation of methane. It may be noted that exothermic methanation reactions are favorable at low temperatures of about 573 K and under experimental conditions. For catalytic deoxygenation of SA under helium, formation of carbon dioxide, carbon monoxide, hydrogen, methane, propane, and higher hydrocarbons were reported [16,29].

3.3. Effects of supports

The effects of supports on HDO of SA were investigated to comprehend role of acidity of supports in the reaction. Accordingly the experiments were designed with nickel supported on three different materials (SiO₂, γ -Al₂O₃, and HZSM-5) of different degree of acidity. The acidity of pure supports and supported nickel catalysts are shown in Table 2. As observed from the table, SiO₂ and γ -Al₂O₃ are almost neutral and HZSM-5 is highly acidic in nature. The nickel supported on γ -Al₂O₃ showed slightly acidic behavior and acidity of catalysts was increased with increasing nickel loading on γ -Al₂O₃ up to 15 wt.%. The increasing acidity may be due to presence of strongly interrelated nickel oxide in the catalysts. The 25NiAl catalyst however showed significantly lesser acidity compared to other γ -Al₂O₃ supported nickel catalysts. It may be due to presence of bulk nickel oxide as confirmed from XRD results as well. The acidity of 10NiZSM catalyst also increased slightly compared to pure HZSM-5. The 10NiSi catalyst was however found to be almost neutral further indicating weak interaction of nickel oxide with silica.

The effects of supports on conversion of SA are shown in Fig. 4. The SA conversions were decreased in the order of $10NiZSM > 10NiAl \sim 10NiSi$. The 10NiZSM catalysts showed about 85% conversion of SA compared to only $\sim 41\%$ for 10NiAl and 10NiSi after 360 min of reaction. The slightly lower reactivity of 10NiSi compared to 10NiAl may be due to poor dispersion of nickel on

Table	3
Effec	s of supports on selectivity to products. ^a

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	100 -	
%	80 -	$- \operatorname{SiO}_{2} - \operatorname{Al}_{2} \operatorname{O}_{3} - \operatorname{HZSM-5}$
stearic acid, 9	60 -	
ersion of	40 -	•
Conve	20 -	
	0 – (0 60 120 180 240 300 360
		Reaction time, min

Fig. 4. Effects of supports on conversion of stearic acid. Conditions: concentration of SA = 0.18 kmol/m^3 , n-dodecane = 100 ml, catalyst loading = 0.5 (w/v)%, temperature = 543 K, initial hydrogen pressure = 8 bars.

 SiO_2 than γ -Al₂O₃ (Table 1). The lesser dispersion of nickel on SiO_2 support is related to poor support-metal interaction that exists between nickel and SiO_2 .

The effects of supports on selectivity to products are shown in Table 3. Highest selectivity to OCTDL was observed with 10NiSi followed by 10NiAl. OCTDL was however not detected in case of 10NiZSM catalyst. On the other hand, maximum selectivity to OCTD was observed for 10NiZSM. From these results it may be concluded that OCTDL formed is transformed instantaneously to OCTD by dehydration followed by hydrogenation reaction in presence of highly acidic catalyst, 10NiZSM. The maximum selectivity to HEPD was observed with nickel supported on γ -Al₂O₃ catalyst. All subsequent studies were conducted using nickel supported on γ -Al₂O₃ catalysts.

3.4. Effects of nickel loadings on γ -Al₂O₃

The catalytic HDO of SA were examined with four different nickel loaded γ -Al₂O₃ catalysts, 5NiAl, 10NiAl, 15NiAl, and 25NiAl under similar experimental conditions. The outcomes of nickel loadings on γ -Al₂O₃ on conversion of SA is shown in Fig. 5. As observed from the figure, SA conversion was increased with increasing nickel loading on γ -Al₂O₃. About 85% conversion of SA was observed for 25NiAl after 360 min of reaction at 543 K. Immer et al. reported about 98% conversion of SA in presence of 0.35 g of 5%Pd/C at 573 K in semi-batch stirred autoclave after 300 min of reaction [16]. The initial reaction rates of SA calculated from experimental data for four different catalysts, 5NiAl, 10NiAl, 15NiAl, and 25NiAl were 2.52 \times 10⁻⁶, 4.06 \times 10⁻⁶, 11.3 \times 10⁻⁶, and 13.0 \times 10⁻⁶ kmol/m³s respectively. About 5.0 times rate enhancement was observed with increasing nickel loading on γ -Al₂O₃ from 5 to 25 wt.%. However, enhancement of reaction rate for increasing

		5 1									
Catalysts	llysts 20% conversion of SA						40% conversion of SA				
	PEND	HEXD	HEPD	OCTD	OCTDL	PEND	HEXD	HEPD	OCTD	OCTDL	
10NiSi	0	1.0	57.3	2.4	39.3	0	1.1	76.6	1.8	20.5	
10NiAl	0	2.3	81.6	0	16.1	0	2.2	90.7	0	7.1	
10NiZSM	0	0	41.9	58.1	0	0	0	39.0	61.1	0	

^a All experimental conditions are same as in Fig. 4.

Catalysts	20% conversion of SA					40% conve	40% conversion of SA			
	PEND	HEXD	HEPD	OCTD	OCTDL	PEND	HEXD	HEPD	OCTD	OCTDL
5NiAl	0	3.9	79.9	0	16.2	-	-	-	-	-
10NiAl	0	2.3	81.6	0	16.1	0	2.2	90.7	0	7.1
15NiAl	0.1	2.3	77.0	1.6	19.0	1.0	2.6	86.0	1.8	8.6
25NiAl	2.4	1.8	45.8	2.1	47.9	1.9	2.3	71.3	2.0	22.6

Table 4 Effects of nickel loadings on γ -Al₂O₃ on selectivity to products.^a

^a All experimental conditions are same as in Fig. 5.

nickel loading from 15 to 25 wt.% was significantly lesser as compared to that of increasing nickel loading from 10 to 15 wt.%. It may be due to presence of bulk nickel in 25NiAl which is relatively less active compared to dispersed nickel for HDO of SA.

The reaction was also conducted in presence of pure γ -Al₂O₃ under identical experimental conditions to establish catalytic role of γ -Al₂O₃ in the reaction. However, no SA conversion was observed even after 360 min of reaction. From this observation it may be concluded that γ -Al₂O₃ alone is playing insignificant catalytic role in HDO of SA. The effects of nickel loadings on selectivity to products for two different SA conversions are shown in Table 4. As observed from the table, selectivity to products was practically remained unaffected up to 15 wt.% nickel loadings on γ -Al₂O₃ for fixed conversion of SA. However, selectivity to OCTDL was found to be higher for 25NiAl compared to other catalysts. About 90% selectivity to HEPD was observed for 25NiAl at 85% conversion of SA. About 98% selectivity to HEPD was reported in presence of Pd/C catalyst at 573 K after 5 h of reaction [16].

3.5. Effects of catalyst loadings

The effects of catalyst loading on conversions of SA were studied for four different 15NiAl catalyst loadings as shown in Fig. 6. As observed from the figure, conversion of SA was increased with increasing catalyst loading. About 75% SA conversion was achieved for 0.75 (w/v)% 15NiAl catalysts loading after 360 min of reaction. The HDO of SA was also studied in absence of any catalysts. However, no conversion of SA was observed even after 360 min of reaction. The effects of catalyst loading on selectivity to products are shown in Table 5. For 0.1 (w/v)% of 15NiAl catalyst loading, HEPD







Fig. 6. Effects of catalyst loadings on conversion of stearic acid. Conditions: concentration of SA = 0.18 kmol/m³, n-dodecane = 100 ml, catalyst = 15NiAl, temper-ature = 543 K, initial hydrogen pressure = 8 bars.

was observed as only product of the reaction even up to 15% conversion of SA at 360 min of reaction. The propensity of formation of other products was increased with increasing catalyst loading keeping HEPD as major product.

3.6. Effects of concentrations of stearic acid

The effects of concentrations of SA on conversion of SA and selectivity to products were studied for three different SA concentrations, 0.11, 0.14, and 0.18 kmol/m³, using 15NiAl as catalyst at 543 K as shown in Fig. 7 and Table 6. The conversion of SA was decreased with increasing concentration of SA. Almost complete conversion of SA was observed for SA concentration of 0.11 kmol/m³ after 360 minutes of reaction. The selectivity to HEPD for fixed conversion of SA remained almost unaffected with increasing SA concentrations as observed from the table. For SA concentrations of 0.18 kmol/m³, about 90% selectivity to HEPD was observed at 50% conversion of SA.

Table 5

Effects of catalyst loadings on selectivity to products.^a

Catalyst loading, (w/v)%	15% conv				
	PEND	HEXD	HEPD	OCTD	OCTDL
0.10	0	0	100	0	0
0.25	0	8.9	50.4	5.8	34.9
0.50	0	2.2	74.1	2.6	21.1
0.75	0	18.5	66.4	0	15.1

^a All experimental conditions are same as in Fig. 6.

Concentration of SA (kmol/m ³)	Concentration of 50% conversion of SA SA (kmol/m ³)				100% conversion of SA					
	PEND	HEXD	HEPD	OCTD	OCTDL	PEND	HEXD	HEPD	OCTD	OCTDL
0.11	1.2	3.6	87.5	1.2	6.5	2.4	5.8	90.3	1.5	0.0
0.14	2.0	1.4	85.1	0.9	10.6	-	-	-	-	-
0.18	1.6	3.5	85.8	1.9	7.2	-	-	-	-	-

Effects of concentrations of stearic acid on selectivity to products.^a

^a All experimental conditions are same as in Fig. 7.



Fig. 7. Effects of concentrations of stearic acid on conversion of stearic acid. Conditions: n-dodecane = 100 ml, catalyst loading = 0.5 (w/v)% 15NiAl, temperature = 543 K, initial hydrogen pressure = 8 bars.

3.7. Effects of temperature

The effects of reaction temperatures on HDO of SA were studied at four different temperatures, 533, 543, 553, and 563 K, using 15NiAl as catalyst. With increasing reaction temperatures, conversion of SA was increased as observed from Fig. 8. About 66%



Fig. 8. Effects of temperature on conversion of stearic acid. Conditions: concentration of $SA = 0.18 \text{ kmol/m}^3$, n-dodecane = 100 ml, catalyst loading = 0.5 (w/v)% 15NiAl, initial hydrogen pressure = 8 bars.

conversion of SA was observed at 533 K after 360 min of reaction; while almost complete conversion of SA was observed at 563 K even after 240 min of reaction. For fixed conversion of SA, selectivity to PEND and HEXD was increased; while selectivity to OCTDL was decreased with increasing temperature as shown in Table 7. The selectivity to HEPD and OCTD was however remained almost constant with increasing reaction temperature. Based on experimental results, initial rate of reaction of SA was calculated at different temperatures and plot of ln(initial rate) versus 1/temperature was made. The apparent activation energy of the reaction was then calculated from slope of best fitted straight line as 205.2 kJ/mol.

3.8. Reproducibility and reusability of Ni/ γ -Al₂O₃ catalyst

In order to demonstrate reproducibility of HDO of SA, three independent experiments (1-3) were conducted under same experimental conditions. The results showed that conversion of SA and selectivity to products was comparable for all three experiments as observed from Table 8. To study reusability of Ni/ γ -Al₂O₃ catalyst, spent catalysts of previous experiments (1 to 3) were first separated by filtration under vacuum and then washed thoroughly with ethanol followed by water for several times. The filtered catalyst was then dried in an oven for overnight at 373 K followed by calcination at 823 K using air for about 6 h. The catalysts were then reduced in a tubular furnace at 973 K under the flow of hydrogen. The regenerated catalyst was then used to study HDO of SA under identical experimental conditions. The conversion of SA and selectivity to products for regenerated catalyst is also shown in Table 8 (expt. no. 4). As observed from the table, regenerated catalyst showed no loss of catalytic activity.

4. Kinetic modeling

The proposed reaction mechanism (Scheme 1) was used to develop an empirical kinetic model for HDO of SA in presence of Ni/γ -Al₂O₃ catalysts. The elimination of both external mass transfer and internal diffusional resistance is very much important for estimation of true reaction kinetics. The independent studies on HDO of SA were therefore conducted under different speed of agitations (1000-2000 rpm) under otherwise similar experimental conditions. The increase in SA conversion with speed of agitation was negligibly small. Therefore, the reaction can be considered as free from external mass transfer resistance. However, resistance due to diffusion of molecules inside the pores could not be evaluated in the present work. Hence kinetic parameters presented in the article include internal diffusional resistance effect, if any. The reactions were considered as first order with respect to liquid phase components. However, the concentration of gas phase hydrogen was not incorporated in kinetic model as excess amount of hydrogen was used in the reaction. Accordingly, rates of formation of different components, stearic acid (SA), heptadecane (HEPD), octadecane (OCTD), pentadecane (PEND), hexadecane (HEXD), and

Table 6

Temperature (K)	50% conversion of SA						95% conversion of SA				
	PEND	HEXD	HEPD	OCTD	OCTDL	PEND	HEXD	HEPD	OCTD	OCTDL	
533	1.5	3.2	82.9	1.9	10.5	-	-	-	-	-	
543	1.6	3.5	85.8	1.9	7.2	-	-	-	-	-	
553	1.7	3.7	85.9	1.9	6.7	4.5	9.6	84.4	1.5	0	
563	3.2	6.1	85.2	2.0	3.5	5.3	10.0	82.9	1.7	0	

Table 7Effects of temperatures on selectivity to products.^a

^a All experimental conditions are same as in Fig. 8.

Table 8

Reproducibility and reusability of Ni/y-Al2O3 catalyst for hydrodeoxygenation of stearic acid.^a

Experiments	Conversion of SA (%) ^b	Selectivity at 50% conversion of SA					
		PEND	HEXD	HEPD	OCTD	OCTDL	
Reproducibility							
1	53.8	1.2	1.8	89.5	0.8	6.7	
2	51.7	1.5	1.5	92	0.4	4.6	
3	53.5	1.7	1.9	90.8	0.7	4.9	
Reusability							
4	52.0	1.5	1.8	89.5	1.3	5.9	

^a Conditions: concentration of SA = 0.18 kmol/m³, n-dodecane = 100 ml, catalyst loading = 0.50 (w/v)% 15NiAl, temperature = 543 K, initial hydrogen pressure = 8 bars. ^b Matching reaction time = 240 min.

Table 9

Rate constants at different temperatures and activation energy (E) and pre-exponential factor (A_0) of the rate constants.

Temperature (K)	Rate constants (s ⁻¹)					RMSE (kmol/m ³)
	k_1	k ₂	k ₃	k_4	k_5	
533	4.20×10^{-05}	3.55×10^{-04}	8.44×10^{-06}	6.03×10^{-06}	1.30×10^{-05}	$9.7 imes 10^{-03}$
543	$6.43 imes 10^{-05}$	$1.52 imes 10^{-03}$	2.43×10^{-05}	1.96×10^{-05}	4.57×10^{-05}	$4.6 imes10^{-03}$
553	1.59×10^{-04}	3.68×10^{-03}	$6.70 imes 10^{-05}$	$1.58 imes 10^{-04}$	$3.37 imes10^{-04}$	$2.8 imes 10^{-03}$
563	3.24×10^{-04}	7.39×10^{-03}	7.59×10^{-05}	5.33×10^{-04}	1.03×10^{-03}	2.2×10^{-03}
E(kJ/mol)	175.4	250.0	190.9	387.7	377.2	
A_0 (s ⁻¹)	5.57×10^{12}	1.34×10^{21}	4.77×10^{13}	$\textbf{5.08}\times10^{32}$	1.08×10^{32}	
	/ i_n	<u>\</u>				

(6)

RMSE = root mean square error =
$$\sqrt{\left(\sum_{i=1}^{i=n} (C_i^{\exp} - C_i^{\operatorname{cal}})^2/n\right)}$$
.

octadecanol (OCTDL) were represented by following ordinary differential equations (Eqs. (1–6)).

$$\frac{\mathrm{d}C_{\mathrm{SA}}}{\mathrm{d}t} = -k_1 C_{\mathrm{SA}} \tag{1}$$

The rate constants of developed model were estimated using experimental data at four different temperatures, 533, 543, 553, and 563 K, by non-linear regression algorithm based on modified Levenberg–Marquardt. The ordinary differential equations of developed model were integrated using fourth order Runge-Kutta method. The following objective function (E) was minimized.

$$E = \sum_{i=1}^{n} \left(\left| \left(C_{\text{SA},i}^{\exp t} - C_{\text{SA},i}^{\text{cal}} \right) \right| + \left| \left(C_{\text{PEND},i}^{\exp t} - C_{\text{PEND},i}^{\text{cal}} \right) \right| + \left| \left(C_{\text{HEXD},i}^{\exp t} - C_{\text{HEXD},i}^{\text{cal}} \right) \right| + \left| \left(C_{\text{OCTD},i}^{\exp t} - C_{\text{OCTD},i}^{\text{cal}} \right) \right| + \left| \left(C_{\text{OCTD},i}^{\exp t} - C_{\text{OCTD},i}^{\text{cal}} \right) \right| + \left| \left(C_{\text{OCTD},i}^{\exp t} - C_{\text{OCTD},i}^{\text{cal}} \right) \right| \right) \right|$$
(7)

$$\frac{\mathrm{d}C_{\mathrm{HEPD}}}{\mathrm{d}t} = k_2 C_{\mathrm{OCTDL}} \tag{2}$$

$$\frac{\mathrm{d}C_{\mathrm{OCTD}}}{\mathrm{d}t} = k_3 C_{\mathrm{OCTDL}} \tag{3}$$

$$\frac{dC_{\text{PEND}}}{dt} = k_4 C_{\text{OCTDL}} \tag{4}$$

$$\frac{\mathrm{d}C_{\mathrm{HEXD}}}{\mathrm{d}t} = k_5 C_{\mathrm{OCTDL}} \tag{5}$$

$$\frac{dC_{\text{OCTDL}}}{dt} = k_1 C_{\text{SA}} - (k_2 + k_3 + k_4 + k_5) C_{\text{OCTDL}}$$

The estimated rate constants at different temperatures are shown in Table 9. As observed from the table, value of rate constants increases with increasing temperature as expected. Arrhenius plot of $\ln(k)$ against 1/T was then made using estimated rate constants at different temperatures as shown in Fig. 9. The activation energy and pre-exponential factor were then obtained from slope and intercept of Arrhenius plot as shown in Table 9. Similar to apparent activation energy, very high activation energies were also observed for all rate constants. The highest activation energy was observed for k₄ and k₅ indicating that formation of PEND and HEXD was dominated at higher temperatures. The concentration of all components involved in the reaction was calculated with time at different temperatures using estimated rate constants. The root mean square errors were then calculated at different temperatures as shown in Table 9. Furthermore, the conversion of SA was calculated and compared with experimental results SA as shown in Fig. 8. Quite a good



Fig. 9. Arrhenius plot of ln(rate constants) versus 1/*T*.

agreement between calculated and experimental conversion of SA was observed.

5. Conclusion

The nickel supported on γ -Al₂O₃, SiO₂, and HZSM-5 catalysts were prepared by incipient wetness impregnation method. Characterization studies revealed that only dispersed nickel oxide (or nickel) was present in γ -Al₂O₃ supported catalysts up to 15 wt.% nickel loading; whereas both bulk and dispersed nickel oxide (or nickel) was observed for 25NiAl, 10NiZSM, and 10NiSi catalysts. Acidity of the supports depends on nickel loading of oxidized catalysts and increases with increasing nickel loading up to 15 wt.%. The performance of the catalysts was examined for HDO of SA in a high pressure batch reactor using n-dodecane as solvent. The supported nickel catalysts demonstrated promising catalytic activity for HDO of SA. HEPD was observed as major product with formation of insignificant quantity of PEND, HEXD, OCTD, and OCTDL. 10NiZSM showed highest catalytic activity followed by 10NiAl and 10NiSi. The nickel supported HZSM-5 catalyst led to formation of OCTD with high selectivity. A comprehensive reaction mechanism was delineated based on products distribution and detailed reaction studies. The conversion of SA was increased with increasing reaction time, nickel loading on γ -Al₂O₃, catalyst loading, and reaction temperature. The conversion of SA was however decreased with increasing concentration of SA. Based on proposed reaction mechanism an empirical kinetic model was developed to correlate experimental concentration versus time data at different temperatures. Quite a good agreement was observed between experimental and calculated conversion of SA.

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