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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 SiO_2, γ-Al_2O_3, 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, H_2 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-Al_2O_3. 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-Al_2O_3 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-Al_2O_3, 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-Al_2O_3 catalyst. An empirical kinetic model was also developed to correlate the experimental data.

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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Nomenclature

HDO	hydrodeoxygenation
HEPD	n-heptadecane
HEXD	n-hexadecane
NiAl	$Ni/\gamma\text{-}Al_2O_3$
OCTD	n-octadecane
OCTDL	l-octadecanol
PEND	n-pentadecane
SA	stearic acid
5NiAl	5 wt.% $Ni/\gamma\text{-}Al_2O_3$
10NiAl	10 wt.% $Ni/\gamma\text{-}Al_2O_3$
15NiAl	15 wt.% $Ni/\gamma\text{-}Al_2O_3$
25NiAl	25 wt.% $Ni/\gamma\text{-}Al_2O_3$
10NiSi	10 wt.% Ni/SiO_2
10NiZSM	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 bio-fuels 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 C_8–C_{24} fatty acids with majority of C_{16} and C_{18} 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], C_{17}-C_{20} and C_{22} 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-Al_2O_3, ZrO_2-CeO_2, Al_2O_3, ZrO_2, CeO_2, SiO_2, 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.% H_2 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 573 K 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% H_2 [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 $Ni/\gamma\text{-}Al_2O_3$ 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 (SiO_2) 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 [$Ni(NO_3)_2{\cdot}6H_2O$, extra pure, ≥97%], SA (SG, ≥97%), and carbon tetrachloride (purity 99.8%) were