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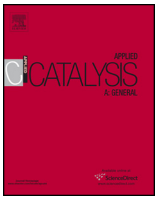

Biofuels production from hydrothermal decarboxylation of oleic acid and soybean oil over Ni-based transition metal carbides supported on Al-SBA-15

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ABSTRACT

Several Ni-based transition metal carbide catalysts supported on Al-SBA-15 were studied for the hydrothermal decarboxylation of oleic acid and soybean oil to produce diesel range hydrocarbons with no added H_2. The effect of pre-reduction, sub-critical, and super-critical water conditions on the catalyst activity and selectivity was investigated. Both the conversion of oleic acid and selectivity of decarboxylation products under super-critical conditions for each catalyst were about two times greater than at sub-critical conditions. In addition, the potential of these catalysts for utilizing aqueous phase reforming (APR) of glycerol for *in situ* H_2 production to meet process demands was demonstrated. The performance of the catalysts increases with the addition of glycerol, especially for the NiWC/Al-SBA-15 catalyst. With the addition of glycerol, the NiWC/Al-SBA-15 catalyst showed greater conversion of oleic acid and selectivity to heptadecane; however, most of the oleic acid was hydrogenated to produce stearic acid. The highest conversion of oleic acid and selectivity for heptadecane was 97.3% and 5.2%, respectively. Furthermore, the NiWC/Al-SBA-15 catalyst exhibited good potential for hydrolyzing triglycerides (soybean oil) to produce fatty acids and glycerol, and then generating H_2 *in situ* from the APR of the glycerol produced. A complete conversion of soybean oil and hydrogenation of produced oleic acid were obtained over the NiWC/Al-SBA-15 at super-critical conditions.

1. Introduction

Biofuels production has been attracting considerable attention because of increases in petroleum prices and the world's energy demand, declines in petroleum reserves, and concerns about the environmental issues associated with greenhouse gas emissions. Triglycerides and fatty acids (from plants, animal fat, and waste oil/grease) can be used as renewable fuel feedstocks [1,2]. Eliminating oxygen from triglycerides and fatty acids in the form of H_2O, CO, or CO_2 produces renewable liquid biofuels that are similar to petroleum fuels and can be directly used in existing infrastructure with no modifications [3,4]. The cost of biofuels production from new vegetable oils is not likely to be competitive with the cost of petroleum fuels. Therefore, using inexpensive and inedible feedstocks such as waste oil and brown grease is necessary to produce biofuels that are fungible with petroleum fuels. The hydrocracking process is the most developed route for removal of oxygen from triglycerides and fatty acids to produce biofuels [5–7]. Our previous study [8] has shown that bimetallic carbide catalysts (NiWC/Al-SBA-15) prepared by a dendrimer-encapsulated-nanoparticles (DENP) method with a Ni–W ratio of 2:1 led to a complete conversion of DDGS corn oil (>95% triglycerides) over 16 continuous days with 100% diesel selectivity for 4 days at 400 °C and 4.48 MPa. However, this process requires high pressure of H_2 and has issues related to catalyst deactivation due to the presence of water [9,10].

An alternative method for removing oxygen is decarboxylation of fatty acid, a method which proceeds under lower H_2 pressure [11]. Most reports have focused on the use of noble metal catalysts, Pd [12–14] or Pt [15–17]. Also, some early studies focused on the decarboxylation of fatty acids in hydrocarbon solvents such as dodecane over Pd-supported catalysts [18–22]. Several studies showed that using water as solvent for the decarboxylation of fatty acids is more advantageous than hydrocarbon solvents [23–25], not

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only because water is an environmentally friendlier solvent but also the avoidance of a water removal step after triglycerides hydrolysis that generates fatty acids in an aqueous stream. Watanabe et al. [26] studied the effect of the addition of alkali hydroxide (NaOH and KOH) and metal oxides (CeO_2, Y_2O_3, and ZrO_2) on the decarboxylation of stearic acid in super-critical water at 400 °C. KOH promoted the monomolecular decarboxylation of stearic acid to produce C_{17} alkane and CO_2, while ZrO_2 was effective for bimolecular decarboxylation into C_{16} alkene and CO_2 because long chain ketone was observed. For the decarboxylation of palmitic acid in sub-critical water at 370 °C, 63% and 76% pentadecane molar yields were obtained over 5% Pd/C and 5% Pt/C, respectively [27]. Although the catalysts experienced a reduction in metal dispersion after the reaction, these changes did not seem to reduce their activities. However, the cost and rapid deactivation due to catalyst coking [19] and lack of H_2 [28] hindered the use of these catalysts commercially.

Fu et al. [29] reported that activated carbons could be an alternative to the expensive noble metal catalysts to convert saturated and unsaturated fatty acids to alkanes in sub- and super-critical water. Although the major products were alkanes that are produced *via* decarboxylation and hydrogenation of oleic acid after 3 h at 370 °C, only 6% molar yield of decarboxylation product was obtained.

Triglycerides, a type of neutral lipids, can be rapidly hydrolyzed in hydrothermal media to produce saturated and unsaturated free fatty acids, as well as glycerol [30]. Some studies examined hydrothermal catalytic reforming of glycerol, commonly referred to as aqueous phase reforming (APR), to generate hydrogen [31–36]. Utilizing glycerol APR for *in situ* hydrogen production can promote the hydrogenation of unsaturated fatty acids. The addition of Re to Pt/C catalyst can motivate the glycerol APR due to the reduction of the affinity for CO [34,37]. A complete conversion of oleic acid was achieved over Pt-Re/C catalyst when a 1:3 glycerol-to-oleic acid molar ratio was applied in a 2 h reaction. The catalyst experienced moderate sintering, suggesting additional work is needed to investigate its hydrothermal stability with time on stream. Vardon et al. [30] proposed an integrated catalytic hydrothermal reaction for the conversion of triglycerides to hydrocarbon fuels with *in situ* hydrogen production from glycerol. A continuous hydrogen supply can be obtained by the APR of glycerol released from triglyceride hydrolysis.

To the best of our knowledge, there has been no study of the hydrothermal decarboxylation of fatty acids over Ni-based transition metal carbide catalysts supported on Al-SBA-15. If sufficiently active, these catalysts could be suitable low cost catalysts for the hydrothermal decarboxylation of fatty acids. Also, unlike noble metal catalysts, these catalysts are not sensitive to CO that is produced during fatty acid decarbonylation [38]. In the present work, we investigate the use of Ni-based transition metal carbide catalysts on an Al-SBA-15 for the decarboxylation in sub- and super-critical water of unsaturated fatty acid (oleic acid) and triglycerides (soybean oil) to produce hydrocarbons in the diesel range without adding hydrogen.

2. Experimental

2.1. Materials

Ammonium (*para*)tungstate hydrate ($H_{42}N_{10}O_{42}W_{12}\cdot xH_2O$, 99.99%, Aldrich), ammonium niobate(V) oxalate hydrate ($C_4H_4NNbO_9\cdot xH_2O$, 99.99%, Aldrich), ammonium molybdate ($H_{24}Mo_7N_6O_{24}\cdot 4H_2O$, Sigma–Aldrich), zirconium(IV) oxynitrate hydrate ($N_2O_7Zr\cdot xH_2O$, 99%, Aldrich), and nickel(II) nitrate hexahydrate ($N_2NiO_6\cdot 6H_2O$, Sigma–Aldrich) were used as W, Nb, Mo, Zr, and Ni sources, respectively. Oleic acid (technical grade 90%), aluminum isopropoxide ($C_9H_{21}AlO_3$, 99.99%), heptane (UN1206, 99%), the mesoporous silica SBA-15, glycerin (Class IIIB) were purchased from Sigma–Aldrich, Aldrich, EMD Chemicals, Advanced Chemicals Supplier (ACS), and Fisher-Scientific, respectively.

2.2. Catalyst preparation

A neutral support, SBA-15, with a 9 nm pore diameter and Brunauer–Emmett–Teller (BET) surface area of 600 m^2/g, was modified by aluminum isopropoxide to adjust its acidity. The advantages of using SBA-15 as a support in this study are its high surface-to-volume ratio, relatively wide pore size to minimize the resistance to triglycerides diffusion, and high thermal stability [39,40]. Moreover, lack of Brønsted acidity allows modifying the acidity of pure siliceous SBA-15 to control the cracking activities [41]. SBA-15 (20 g) was suspended in hexane (150 mL); then, aluminum isopropoxide (0.067 g) was added to the solution and stirred for 24 h. The mixture was filtered, dried, and calcined at 550 °C for 4 h. According to our previous work [8], the catalysts NiNb, NiMo, NiW, and NiZr were prepared in the ratio of 6.67 wt% Ni:3.33 wt% M (M = Nb, Mo, W, Zr) by the wet co-impregnation of aqueous solutions of ($Ni(NO_3)_2\cdot 6H_2O$, $C_4H_4NNbO_9\cdot xH_2O$), ($Ni(NO_3)_2\cdot 6H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2$), ($Ni(NO_3)_2\cdot 6H_2O$, $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$), and ($Ni(NO_3)_2\cdot 6H_2O$, $ZrO(NO_3)_2\cdot xH_2O$) on the modified Al-SBA-15 support. The resulting solids were dried and calcined at 450 °C for 4 h.

Carburization was conducted using temperature-programmed reduction (TPR) according to the method of Claridge et al. [42]. Each metal oxide precursor was placed in a quartz tube and subjected to a flow of 20% CH_4/80% H_2 at 30 cm^3/min and a heating rate of 10 K/min to 250 °C, followed by 2.0 K/min to 730 °C. The temperature was maintained at 730 °C, the optimal temperature for carbide formation, for 30 min to complete the reaction [42]. After cooling, the catalyst was passivated under a mixture of 1% O_2 in Ar for 1 h to eliminate its pyrophoricity [43] and protect the bulk of the catalyst against deep oxidation [44].

2.3. Material characterization

X-ray diffraction (XRD) patterns were collected using a Rigaku RU2000 rotating anode powder diffractometer (Rigaku Americas Corporation, TX) with SmartLab Guidance and MDI Jade 8 software at a scan rate of 8°/min. Scanning electron microscopy (JSM-7600 FE SEM) equipped with Pegasus Apex 2 integrated EDS and EBSD systems with capabilities of spectral imaging, OIM data collection and analysis with high accuracy and high efficiency was used to determine the composition of the catalysts.

2.4. Reaction procedure

The catalytic hydrothermal decarboxylation of oleic acid was conducted in unstirred mini-reactors assembled from 3/8-inch stainless steel Swagelok parts, sealed with a cap on each end to give a reactor volume of 1.52 mL [27]. The advantage of using 316L stainless steel reactors to carry out the reaction under sub- and super-critical water is the high contents of Cr and Ni [45]. The protective Cr_2O_3 layer on the steel surface prevents the metal leaching. The 316L stainless steel reactor shows good stability when it was exposed to supercritical water at 480 °C/25 MPa for 120 h. Prior to use in any experiments, the reactors were washed with acetone and water to remove any residual materials. In typical experiments, 10 mg catalyst, 0.642 mL water, and 0.156 mmol oleic acid were loaded in the reactors. The reactors were sealed in a glove box to avoid their exposure to air. The loaded reactors were placed in a pre-heated furnace (400 °C) and (350 °C) to achieve super-critical and sub-critical conditions, respectively. After the desired reaction time was completed (4 h), the reactors were submerged in a water