



Supported iron nanoparticles for the hydrodeoxygenation of microalgal oil to green diesel



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ABSTRACT

Iron nanoparticles supported on mesoporous silica nanoparticles (Fe-MSN) catalyze the hydrotreatment of fatty acids with high selectivity for hydrodeoxygenation over decarbonylation and hydrocracking. The catalysis is likely to involve a reverse Mars–Van Krevelen mechanism, in which the surface of iron is partially oxidized by the carboxylic groups of the substrate during the reaction. The strength of the metal–oxygen bonds that are formed affects the residence time of the reactants facilitating the successive conversion of carboxyl first into carbonyl and then into alcohol intermediates, thus dictating the selectivity of the process. The selectivity is also affected by the pretreatment of Fe-MSN, the more reduced the catalyst the higher the yield of hydrodeoxygenation product. Fe-MSN catalyzes the conversion of crude microalgal oil into diesel-range hydrocarbons.

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1. Introduction

The increasing energy demand and concerns over the gradual depletion of fossil fuels have attracted significant amount of research to the exploration of alternative energy sources [1,2]. In this context, microalgae are considered as one of the most promising renewable energy resources owing to their short harvest cycle, small cultivation area, high lipid content (up to 80% of their dry weight), and minimum greenhouse gas emission [3,4].

The major components of microalgal oil are free fatty acids (FFAs) and triglycerides. These can be converted to fatty acid methyl esters (FAMES) by catalytic reaction with methanol and used as biodiesel. However, due to the degree of unsaturation and high oxygen content of the FAMES, issues such as poor storage stability, marginal cold flow, and engine compatibility limit their widespread use [5,6]. An alternate technology to produce biofuels from microalgal oil is through hydrotreating with Ni, Co, and Mo sulfides or noble metal catalysts such as Pd and Pt supported on metal oxides [7–14]. While the high price of the noble metals can be avoided by using the sulfided catalysts, slow desulfurization reduces their activity and contaminates the fuel [7,9,15]. Furthermore, these catalysts have shown poor selectivity, favoring cracking and decarbonylation over hydrodeoxygenation to produce broad hydrocarbon distributions [16]. In an effort to establish a

more economical sulfur-free catalyst to upgrade renewable oils, Lercher has demonstrated the hydrodeoxygenation of microalgae oil to alkanes by cascade reactions on bifunctional catalysts based on Ni and an acidic zeolite [14,17]. Following work by the same group illustrated the selectivity toward decarbonylation route by supporting Ni catalyst on ZrO₂ which directed the conversion through two parallel pathways [18].

The success of Ni in the conversion of renewable feedstocks into green diesel [14,19,28] stimulates the exploration of other inexpensive transition metals as catalysts for the process. Considering its rich redox-chemistry, high natural abundance and low price, iron emerges as an appealing candidate for this kind of conversion. While many researchers have been studying iron catalysts in the Fischer–Tropsch synthesis for several decades [20,21], the activity and selectivity of these species for the hydrodeoxygenation of fatty acids has not been much explored. To contribute to the efforts for economical and efficient catalysts for upgrading renewable feedstocks to green diesel, we report the synthesis of iron nanoparticles supported on mesoporous silica nanomaterials (Fe-MSN), and their application in the hydrotreatment of fatty acids and crude microalgal oil.

2. Experimental

2.1. Materials

Pluronic P104 (>99.8%) was generously provided by BASF. Tetramethyl orthosilicate (TMOS, 98%), oleic acid (≥99.0%) and

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Sylon (N,O-bis(trimethylsilyl)trifluoroacetamide, 99.3% and trimethylchlorosilane, 99.3%, 99:1) were purchased from Sigma Aldrich. Iron (III) Nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] (100%), hydrochloric acid (37.3%, ACS certified) and hexanes (certified, mixture of isomers, boiling range 1.0 °C) were purchased from Fisher Scientific. All reagents were used as received without further purification.

2.2. Catalyst preparation

MSN was prepared using a nonionic block co-polymer Pluronic P104 surfactant [22]. In a typical synthesis, P104 (7.0 g) was dissolved in aqueous HCl (273.0 g, 1.6 M). After stirring for 1 h at 56 °C, tetramethylorthosilicate (TMOS, 10.64 g) was added and stirred for additional 24 h. The resulting mixture was further hydrothermally treated for 24 h at 150 °C in a high-pressure reactor. Upon cooling to room temperature, the white solid was collected by filtration, washed with copious amounts of methanol, and dried in air. To remove the surfactant P104, the MSN material was heated at a ramp rate of 1.5 °C min⁻¹ and maintained at 550 °C for 6 h. MSN was then mixed with water and stirred at room temperature in order to rehydrate and regenerate the silanol groups, followed by filtration and drying. For impregnation, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.40 mmol, 0.16 g) was completely dissolved in water (0.48 mL). To this solution, the rehydrated MSN (0.4 g) was added and mixed. The solid mixture was calcined in air at a heating rate of 10 °C min⁻¹ to 300 °C and maintained at that temperature for 3 h followed by reduction at 400 °C for 6 h in a constant flow of H_2 (1.67 mL s⁻¹).

2.3. Characterization

Surface analysis of the catalyst was performed by nitrogen sorption isotherms at -196 °C in a Micromeritics Tristar analyzer. The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method. Pretreatment of samples for surface area measurement was done by flowing N_2 for 6 h at 100 °C. Powder X-ray diffraction patterns were obtained with a Rigaku Ultima IV diffractometer using Cu target at 40 kV and 44 mA, and samples were analyzed in the 0.8–90 2 θ° at a scan rate of 1 2 θ° min⁻¹. Cu K β was removed using a monochromator. Crystallite size was estimated from modeling the diffraction at 44.6 2 θ° with OriginPro software and incorporating the FWHM into the Scherrer equation ($d = K\lambda/\beta\cos\theta$, where d is the estimated crystallite size, K is the shape factor, λ is the wavelength of the Cu K α , β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle) [27]. For transmission electron microscopy measurements, an aliquot of the powder was sonicated in methanol for 15 min. A single drop of this suspension was placed on a lacey carbon-coated copper TEM grid and dried in air. The TEM examination was completed on a Tecnai G2 F20 electron microscope operated at 200 kV. Average particle size was calculated using ImageJ software based on five representative TEM images (100 particles). Fourier transform infrared (FT-IR) spectra were recorded on Nicolet Nexus 470. Samples were diluted with KBr (about 5 wt%) and made into pellets for analysis in transmission mode. To measure the Fe loading, samples (2.0 mg) were digested for 20 h in aqueous HF and HCl solution (0.18% and 5% respectively) and analyzed in a Perkin Elmer Optima 2100 DV ICP-OES. Temperature-programmed reduction was performed in a Micromeritics AutoChem II using a flow of H_2 in Argon (10.13%, 50 mL min⁻¹) ramping from 40 °C to 500 °C at a rate of 10 °C min⁻¹. XPS analysis was done with a PHI 5500 multi-technique system using a standard Al X-ray source. Since the samples were mounted on two-sided scotch tape, charge correction was

accomplished by shifting the spectra so that silicon 2p peak was at 103.3 eV.

2.4. Catalytic activity measurements

All catalytic reactions were performed in a 100-mL batch reactor (Parr Instruments). In a typical experiment, the catalyst (10 mg) and oleic acid solution in hexanes (1 mM, 10 mL) were added in the reactor. The reactor was purged three times with H_2 and was then pressurized with H_2 to 30 bar at ambient temperature. For kinetics study, the reaction was carried out at 290 °C for 1, 2, 3, 4, 5, and 6 h with constant stir rate (500 rpm). The reaction was allowed to cool to room temperature and the catalyst was separated. The reaction product was mixed with 1 mL Sylon (N,O-bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane, 99:1) and heated to 70 °C for 2 h for further derivatization. The final mixture was analyzed in an Agilent GC-MS (7890A, 5975C) with a HP - 5MS column. Runs started at 100 °C for 5 min, then ramped to 200 °C at a rate of 20 °C min⁻¹ held for 25 min, and then ramped to 280 °C at 20 °C min⁻¹ holding for 5 min at this temperature. Methyl nonadecanoate was used as an internal standard. Conversion was defined as mole% and calculated as moles of converted oleic acid per mole of starting oleic acid times 100%. Yields were defined as mole% and were calculated as moles of each product per mole of starting oleic acid times 100%.

Similar experiment was conducted on crude microalgal oil obtained from Solix Biofuels, Inc. by adding Fe-MSN catalyst (10 mg) to a solution of microalgal oil (10 mg in 10 mL hexanes) and heating to 290 °C under 30 bar H_2 for 6 h.

3. Results and discussion

3.1. Synthesis of Fe-MSN

The textural properties of MSN support and Fe-MSN catalyst are summarized in Table 1. ICP measurement indicated that 6.0 wt% Fe was immobilized on the MSN. Formation of the Fe nanoparticles led to approximately 10% decrease in the surface area and pore volume of the support; however, its nitrogen sorption isotherm remained type IV confirming retention of the mesoporous character (Fig. 1a) [23]. TEM and STEM imaging suggested that the Fe nanoparticles were located mainly inside the pores of MSN (Fig. 1b). Low-angle XRD analysis confirmed that the structure of the support was not affected by the formation of Fe nanoparticles, as it preserved the $p6mm$ pattern characteristic of SBA-15 type materials (Fig. 1c) [24]. Wide-angle XRD showed a pattern of peaks corresponding to the body-centered cubic phase of crystalline iron nanoparticles (JCPDS card No. 89-7194, Fig. 1d) [25,26]. The wide reflections indicated small crystallite size of the iron nanoparticles. Estimation using Scherrer equation indicated that their size (9.9 nm) was similar to the width of the mesopores (10.9 nm), suggesting nanoparticle growth was restricted by pore width [27]. This observation was supported by estimation of the average size of the Fe nanoparticles from TEM images (10.7 nm), which was only slightly smaller than the pore width (Fig. S1).

Table 1
Textural properties of the support and catalyst.

Material	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
MSN	331	0.97	11.1
Fe-MSN	295	0.88	10.9

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