Sulfur-free Ni catalyst for production of green diesel by hydrodeoxygenation

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Sulfur-free Ni supported on H-Y zeolites, γ-Al$_2$O$_3$ and SiO$_2$ synthesized by the wet impregnation method, and Pd/C were tested in hydrodeoxygenation (HDO) of stearic acid. The catalysts were forming n-heptadecane except Ni/H-Y-80, which was producing n-heptadecane and n-octadecane. Ni/H-Y 80 and Pd/C were tested on HDO of fatty acid methyl esters from chlorella, tall oil fatty acids, and animal fat. The reactions converting the substrates to the final products followed the path from unsaturated esters to acids, with hydrogenation of the latter into alcohols (i.e., stearyl alcohol), and finally formation of hydrocarbons. Ni/H-Y-80 permitted rapid and complete conversion into hydrocarbons, while Pd/C displayed 5–20 times lower turnover frequency, producing saturated intermediates along with hydrocarbons. The catalyst reusability of Ni supported on Y zeolites was studied by recycling and regenerating the spent catalyst from fatty acid HDO. The catalysts demonstrated the possibility of restoring the rates per unit of surface area after regeneration. Catalysts used in HDO of different feedstocks were investigated by thermogravimetric analysis, inductively coupled plasma-optical emission spectroscopy, transmission electron microscopy, surface area measurements, and pore size analysis.

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1. Introduction

Fossil fuel resources are being depleted and the world is gradually adapting to this new paradigm [1]. Biodiesel is a notable alternative to petroleum-derived diesel; however, substituting the latter would take decades, since the production of biodiesel is very small compared to that of petrodiesel. The cost of biodiesel is one disadvantage leading to limited commercial application, even though it has several advantages; the price of raw material constitutes 70–95% of the total biodiesel cost [2–4]. Different possibilities of biodiesel production from biomass resources have been explored in recent years. Biofuel feedstock includes agricultural corps, plant material, animal byproducts, and recycled waste. It is crucial that feedstock for biodiesel production, besides being low-cost, should not compete with food resources.

In order not to compete with edible vegetable oils, low-cost profitable biodiesel should be produced from low-cost feedstocks such as nonedible oils, animal fat, soap stocks, and greases. However, the availability of these feed sources is not sufficient to

match present-day demands for biodiesel, which are experiencing fast growth. For example, biomass energy consumption in the United States grew more than 60% from 2002 to 2013 [5]. In general, the feedstock for biodiesel production can be divided into four groups: vegetable oils (edible and nonedible), animal fats, used cooking oils, and algae [6].

Algae are considered a potential feedstock for second-generation biodiesel. Microalgae do not compete with food resources, as they can be cultivated in open ponds on nonarable lands using sidestream water and CO$_2$. They have a higher growth rate than land crops, requiring much less area than other biodiesel feedstocks of agricultural origin. In 2006, worldwide aquacultural macroalgae production was estimated to be approximately 15.1 million tons (worth about €5.4 billion) [7]. In 2011, Norsker et al. [8] estimated algae production cost to be 400 €/1000 kg, while the value of algae biomass is 1650 €/1000 kg. Algae are firmly recognized as a potential source for direct production of bioenergy, food, pharmaceuticals, and nutraceuticals [9,10]. Nowadays, microalgae are seen as an alternative feedstock for biodiesel production, being the target of a large number of consortia, private and public organizations that are investing in R&D aiming at the most effective and cheapest technology for producing large

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amounts of algal oil [11]. *Chlorella* algae contain fatty acid methyl esters (FAME), typically a mixture of saturated and unsaturated fatty acids [12].

Tall oil fatty acid (TOFA) is a byproduct of the pulp and paper industry. The use of TOFA as a feedstock for the production of biodiesel is of great interest, since it does not compete with food production and has the potential to be used in hydrodeoxygenation (HDO) processes. In Europe, especially Finland and Sweden, utilization of tall oil for fuel has been popular, given the vast availability of the feedstock. The two countries provide 90% of total EU production and 80% of EU consumption of tall oil, according to industry sources. One big producer in Sweden is Sunpine, which started producing 830 ktons/yr of tall oil-based biodiesel in mid-2010 in Pitea [13]. Tall oil is used in various applications, such as paints and coatings, biolubricants, and performance polymers, and can also be used in pharmaceuticals and health-enhancing food additives. In the biofuels industry, tall oil fatty acids mainly with 18-carbon chains are used as a feedstock for green diesel production. These acids undergo oxygen removal and saturation to be converted at the end into *n*-heptadecane and/or *n*-octadecane. In Finland, there is production of green diesel from TOFA on an industrial scale by UPM [13,14].

Waste animal fat is a promising cheap alternative feedstock for the production of biodiesel that does not compete with food resources. In addition, the use of animal fat is considered profitable because these fats frequently offer an economic advantage over plant crops, often being favorably priced [15]. Animal fat is a completely renewable source of energy. It is biodegradable, nontoxic, and safe to use in diesel engines without modification. Multiple animal fat feedstocks for biodiesel fuels are making animal fat-based biodiesel of high quality. In the United States, the meat production system produces nearly 10,000 tons of a byproduct in the form of various types of fats and proteins [16]. Animal fats consist essentially of fatty acid triglycerides.

A number of catalytic methods have been established for upgrading biomass feedstock into biofuels. These routes include HDO over sulfided catalysts such as alumina-supported NiMo and CoMo [17–22], or over noble metals namely palladium and platinum catalysts [20,21,23–27], as well as cracking and catalytic pyrolysis [28–30]. HDO is an attractive method that has been widely used for conversion of fatty acids into green diesel. In previous studies [31–33], palladium supported on carbon was demonstrated to be the best catalyst for deoxygenation of fatty acids. Noble metals are advantageous since they have high activity without a need for sulfidation. However, they are less economically attractive than nickel.

In this work, we have synthesized Ni catalysts supported on H-Y, γ-Al$_2$O$_3$, and SiO$_2$ by wetness impregnation and compared their catalytic performance in HDO of stearic acid (model compound of fatty acids) to produce diesel-range hydrocarbons with that of Pd supported on active carbon. HDO of four feedstocks was thereafter investigated over Ni/H-Y and Pd/C in order to determine activity with different substrates. Reuse of these catalysts has been also studied. The properties of the catalysts were characterized by various physicochemical methods.

2. Experimental

2.1. Catalyst preparation

A wetness impregnation evaporation method was used for the preparation of 5 wt.% Ni (Fluka, 98%) on SiO$_2$ (Silica Gel, Merck), sieved H-Y-80 zeolites (Zeolyst International, SiO$_2$/Al$_2$O$_3$ = 80), and γ-Al$_2$O$_3$ (Versal Alumina VGL-25, UOP) with a size below 63 μm. H-Y support was calcined in air at 400 °C for 4 h, followed

by sieving. Thereafter, nickel(II) nitrate hexahydrate was dissolved in 100 ml deionized water, giving a pH equal to 6.1, followed by addition of 10 g of H-Y to the solution, resulting in a decrease of pH to 3.2. The mixture remained under continuous stirring for 24 h in a 60 °C oil bath before water was evaporated and impregnation of Ni on the zeolites was permitted. Thereafter, the catalyst was dried overnight at 100 °C and then calcined at 400 °C for 3 h. Similar methods were used to synthesize 5 wt.% Ni/γ-Al$_2$O$_3$ and 5 wt.% Ni/SiO$_2$. A quantity of 5 wt.% Pd/C (20,568-0) was purchased from Sigma-Aldrich.

2.2. Catalyst characterization methods

The specific surface area of the catalysts was measured by nitrogen physisorption using a Sorptometer 1900 apparatus (Carlo-Erba Instruments). Prior to measurements, the fresh samples and those spent in HDO of FAME and TOFA were outgassed at 150 °C for 3 h, and the catalysts spent in HDO of animal fat were outgassed at 300 °C for 6 h. The specific surface area was determined using the BET equation, while the pore diameter was determined using the Barrett-Joyner-Halenda method [34]. The spent catalysts were collected, washed with acetone, and dried at 70 °C for 24 h prior to nitrogen adsorption analysis.

Reduction temperature was determined by temperature-programmed reduction (TPR) performed with an Autochem Micrometrics 2910. The catalysts were kept overnight in an oven at 100 °C; thereafter, around 100 mg of the sample was loaded into a U-shaped quartz tube and heated to 650 °C at a constant rate of 10 °C/min in the hydrogen reductive medium.

Palladium dispersion was measured by pulse CO chemisorption with an Autochem 2910 apparatus with 10% CO in 90% He. Prior to measurements, the sample was kept overnight at 100 °C, and thereafter reduced in hydrogen at 250 °C for 2 h at 5 °C/min prior to the analysis. The sample was then flushed with inert gas for 30 min. The pulse chemisorption was performed in a water bath at a monitored temperature. The stoichiometry CO:Pd was assumed to be 2:1.

Acid and basic properties of nickel supported on H-Y and the parent H-Y were determined by ammonia and carbon dioxide temperature-programmed desorption (TPD), respectively, performed with an Autochem Micrometrics 2910. The catalyst and the bare support were kept overnight in an oven at 100 °C prior to the analysis. The sample was heated in He to 300 °C at a rate of 30 °C/min and kept at this temperature for 10 min, after which it was cooled down and flushed with helium, followed by heating to 100 °C. The measurements began with the increase of temperature to 900 °C with a heating ramp of 20 °C/min, which remained constant for 30 min.

The morphology and crystal size distribution of fresh and spent Ni supported on H-Y samples were studied by a scanning electron microscope (Zeiss Leo 1530 Gemini) equipped with a Thermo-NORAN vantage X-ray detector. An average of 200 particles were counted for the crystal size distribution. Energy-dispersive X-ray analysis (EDXA) was carried out with the same instrument.

Nickel and palladium particle size distributions were measured from images obtained by a JEM-1400 plus TEM (transmission electron microscope, voltage 120 kV). The samples were dissolved in ethanol in an ultrasonic bath, and 100 μl of the suspension was fixed on a carbon film-grid. An average of 200 particles were counted for the particle size distribution.

Thermogravimetric analysis (TGA) was carried out to measure coke formed on the spent catalysts. A CHAN D-200 instrument was used to monitor real-time weight loss as a function of time. A quantity of 45 mg was loaded into a quartz holder and burnt at up to 600 °C in air with the heating rate of 5 °C/min to 450 °C,