



Preparation and characterization of alumina supported nickel-oxalate catalyst for the hydrodeoxygenation of oleic acid into normal and iso-octadecane biofuel



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ABSTRACT

In this study, nickel II oxalate complex (NiOx) was prepared by functionalization of nickel with oxalic acid (OxA) and incorporated into Al₂O₃ to synthesize alumina supported nickel oxalate (NiOx/Al₂O₃) catalyst for the hydrodeoxygenation (HDO) of oleic acid (OA) into biofuel. The synthesized NiOx/Al₂O₃ was characterized and the X-ray fluorescence and elemental dispersive X-ray results showed that NiOx was successfully incorporated into the structure of Al₂O₃. The X-ray diffraction and Raman spectroscopy results confirmed that highly dispersed Ni species are present in the NiOx/Al₂O₃ due to the functionalization with OxA. The catalytic activity of the NiOx/Al₂O₃ on the HDO of OA produced a mixture of 21% iso-C₁₈ and 72% n-C₁₈ at a 360 °C, 20 bar, 30 mg NiOx/Al₂O₃ loading pressure and gas flow rate of 100 mL/min. The presence of i-C₁₈ was ascribed to the OxA functionalization which increased the acidity of NiOx/Al₂O₃. The NiOx/Al₂O₃ reusability study showed consistent HDO ability after 5 runs. These results are promising for further research into biofuel production for commercialization.

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1. Introduction

The search for alternative source of energy has been intensified in recent times since the sources of fossil fuels is fast depleting and the exhaust from combustion engines has many serious negative effects on the environment. Even the global politics and peace has also been affected by fossil fuel. This search has led to the identification and researches into renewable and sustainable fuels of bio-origin such as biofuel which is efficient, cost-effective and reduces the vehicular emissions [1]. Biofuel is chemically and structurally different from the famous biodiesel which is a product of transesterification process of triglycerides with methanol. In view of biodiesel high cloud and pour point which can lead to clogging of fuel filters and supply lines at low temperatures, it is considered inferior compared to biofuel [2,3]. In addition, the presence of O₂ in the biodiesel molecules lowers its energy density by about 9–13% as compared with the conventional diesel fuels, and its chemical instability limits its storage without additives which invariably increases the production and storage costs [3,4]. Similarly, glycerol which is a by-product of the transesterification

process has not found a matching market hence creating a storage handling menace [4]. In the production of biofuel, hydrodeoxygenation (HDO) of the feed stocks such as triglycerides has been identified a veritable option compared to decarboxylation and decarbonylation processes (Decarbs). This is because HDO products are pure paraffin with constituents and chemical properties matching close to those found in petroleum diesel fuel unlike mixtures of paraffin and other condensation products such as esters and ketones observed in Decarbs which adversely reduces the energy density [2,3].

Currently, the most researched area of the HDO process is the catalyst synthesis since the process can be adapted to the existing conventional crude oil refinery facilities which in turn would minimize the capital cost [3]. Several attempts have since been made to synthesize various catalysts such as single metals like Pt/Al₂O₃ [2], Pd/C [5] and Pt/Zeolite [6] similarly, bimetallic supported catalysts like NiMo/γAl₂O₃ and CoMo/γAl₂O₃ [6,7] had been synthesized to produce high cetane index renewable biofuel and the bimetallic catalysts displayed higher activities. In order to introduce isomerization ability to the catalysts activities, additives such as sulfur had been introduced during the synthesis stage [6]. The sulfurized NiMo/γAl₂O₃ exhibited production of high iso-paraffin contents as well as comparable higher HDO activities

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which were ascribed to the catalyst increased acidity. Actually, iso-paraffins are biofuel value-added-components because they reduced the biofuel freezing point by about 12 °C which in turn improved the biofuel cold flow property such as the cold flow filter point [3]. In view of the environmental effect of sulfur on the environment, Kovacs et al, [3] increased the acidity of NiMo/Al₂O₃ using fluorine and they reported exceptional degree of paraffin skeletal isomerization. Recent studies [8] reported the functionalization of Ni and Mo with urea in order to achieve organometallic catalysts that are known for their higher reactivity and stability. The result showed that urea improves the metals dispersion and solubility in the γ -Al₂O₃ support which in turn enhances its morphology and textural properties leading to the formation of highly reactive octahedral molybdenum and nickel oxides with proper acidity. A recent patent [9] also reported the comparably higher overall efficiency of oxalate functionalized catalyst over their metal oxide counterparts. Their findings agree with our earlier report [10] on organo-functionalization of Fe using oxalic acid to develop the highly reactive ferrioxalate catalyst.

In view of the aforementioned reviews, this study investigates the applicability of an expediently synthesized Al₂O₃ supported organo-functionalized Ni with oxalic acid to form nickel-oxalate with increased acidity for HDO and paraffin skeletal isomerization of oleic acid into high grade biofuel. Prior to the catalytic activity test, the catalyst was characterized for the physical and chemical properties.

2. Experimental

2.1. Materials

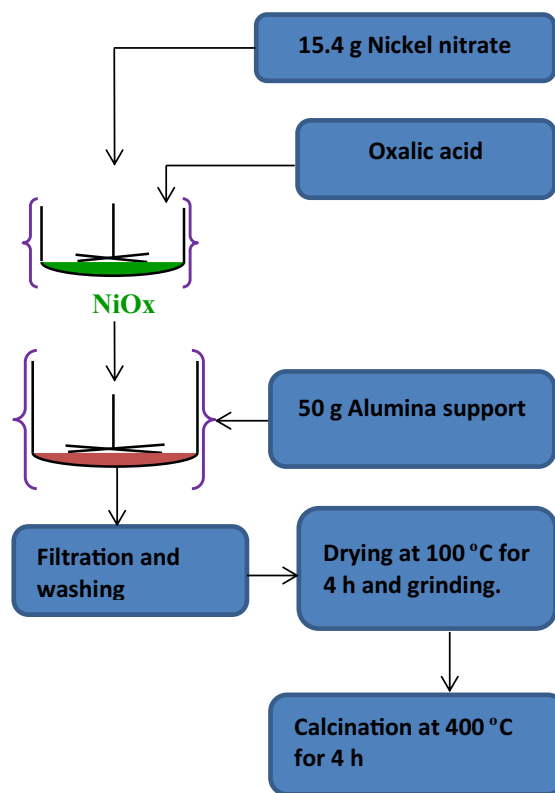
Nickel nitrate hexahydrate and anhydrous oxalic acid were purchased from Sigma–Aldrich. Synthesis grade alumina (Scharlau AL0830, 80%) and all materials were used without any pretreatment.

2.2. Catalyst development

Nickel oxalate catalyst was prepared via functionalization of 15.4 g nickel nitrate (oven dried at 100 °C for 3 h) with stoichiometric ratio of oxalic acid (OxA) to yield the polynuclear nickel II oxalate complex (NiOx) in an aluminum foil wrapped conical flask due to the high photo sensitivity index of metal oxalate ligands [10]. The NiOx was subsequently incorporated into alumina support using simple dissolution method [9–11]. The synthesized nickel oxalate alumina supported (NiOx/Al₂O₃) catalyst was dried in the oven at 100 °C, grinded and calcined at 400 °C for 4 h followed by characterization and testing. The NiOx/Al₂O₃ synthesis scheme is shown in Scheme 1.

2.3. Catalyst characterization

X-ray fluorescence (XRF) analysis of the samples were done using a micro-X-ray micro-EDX 100 Schmadzu, NY and X-ray tube of rhodium anode and scintillation detector operating on a 40 mA current and 40 mV voltage to obtain the samples spectra. Energy dispersive X-ray (EDX) and Scanning electron microscopy (SEM) were performed to determine the samples elemental composition and morphology, respectively using (Model EMJEOL- JSM6301-F) with an Oxford INCA/ENERGY-350 microanalysis system. Nitrogen adsorption–desorption measurements (BET method) were performed at liquid nitrogen temperature (–196 °C) with an autosorb BET apparatus, Micromeritics ASAP 2020, surface area and porosity analyzer to determine the surface area, pore size and structure, and the pore volume. Before each measurement, the samples were first degassed at 350 °C for 2 h and thereafter kept at liquid nitrogen



Scheme 1. Summary of NiOx/Al₂O₃ preparation steps.

temperature to adsorb nitrogen. X-ray diffraction (XRD) patterns of the samples were measured with Philip PW 1820 diffractometer to determine the crystal phase and structure of the metal oxides earlier detected by XRF/EDX analyses. Fourier transformed infrared (FTIR) spectroscopy analyses were performed on the samples to determine the functional groups present in order to understand the chemistry of the synthesized catalyst with respect to the support. The instrument used is Perkin–Elmer Spectrum GX Infrared Spectrometer with resolution of 4 cm^{–1} operating in the range of 4000–400 cm^{–1}. The Raman spectra of the samples were obtained with a Spex Triplemate spectrograph coupled to a Tracor Northern 1024 large area intensified diode array detector.

2.4. Oleic acid deoxygenation experiments

Hydrodeoxygenation (HDO) of oleic acid (OA) was conducted using a 100 mL high pressure semi-batch reactor. The reaction temperature and NiOx/Al₂O₃ loading were varied within 320–380 °C and 10–40 mg, respectively at an earlier predetermined reaction pressure of 20 bar and 100 mL gas flow rate (90 vol% N₂ and 10 vol% H₂). The flow of carrier gas and reaction pressure inlet and outlet were controlled by a flow (Brooks 58505 S) and a pressure controller (Brooks 5866), respectively. In a typical experiment, and 40 g (~45 mL) of OA was added to the reactor followed by the required quantity of calcined NiOx/Al₂O₃ and the catalyst was reduced in situ under flowing H₂ at 200 °C for 1 h prior to use after which the reactor was purged with He. The operating temperature was established and monitored by a type-K Omega thermocouple placed inside the reactor. Before the HDO reaction was initiated, 100 mL/min of 90 vol% N₂ and 10 vol% H₂ was passed through the reactor until the desired reaction pressure was reached and the reaction commences by turning on the stirrer at a speed of 2000 rpm. Based on preliminary studies, all experiments were performed under 60 min and the reactor set up was cooled by forced air before

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