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On the production of bio-hydrogenated diesel over hydrotalcite-like supported palladium and ruthenium catalysts

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ABSTRACT

Jatropha oil is a non-edible and promising feedstock for the manufacturing of renewable diesel by the process of catalytic hydrotreatment. The present work focuses on the production of diesel range hydrocarbons over hydrotalcite-like (HTlc) materials promoted with Pd and Ru. Catalytic activities of the materials were investigated in a trickle-bed reactor. The performance of these catalysts was assessed by studying the influence of various operating parameters like temperature, WHSV, pressure and H_2/oil ratio. Our lab-made materials exhibited encouraging performance in terms of jatropha oil conversion and C_{15}-C_{18} hydrocarbon yield. The maximum oil conversion was achieved at optimized reaction conditions, i.e. 91.2% with Pd and 85.6% with Ru catalyst. These results justify the impregnation of noble metals over HTlc-based materials owing to their high activity in hydrogenation. Both Pd/HTlc and Ru/HTlc catalysts remained stable for over 30 h.

1. Introduction

The current global climatic change coupled with issues of energy security act as driving forces for the adoption of bio-based fuels. Bio-hydrogenated diesel (BHD), a second generation biofuel, made from vegetable oil and fats, is a potential alternative to fossil fuels owing to its eco-friendly and non-polluting nature. Straight chain hydrocarbons containing 15 to 18 carbon atoms are the major components of BHD. It can be produced by catalytic hydrotreatment of vegetable oils at elevated temperature and pressure. In this process of hydrotreatment of vegetable oils, triglycerides undergo saturation followed by hydrogenolysis, which leads to the formation of fatty acids and propane. In the next step, fatty acids are transformed into n-alkanes (C_{15}-C_{18}) by deoxygenation reactions. To improve the cold flow properties of the BHD, these n-paraffins isomerize to their branched isomers [1]. High-energy content, low production cost, low emissions and high process flexibility are the major advantages associated with BHD. Besides, properties of BHD are comparable with that of petroleum-based diesel. Many comprehensive studies on hydroprocessing of vegetable oils were reported in the literature. The studies were performed with a variety of feedstocks. The feed oils used were jatropha oil [2–8], sunflower oil [9–12], rapeseed oil [13–15], palm oil [6,16], cottonseed oil [17], karanja oil [18], canola oil [6], waste cooking oil [19,20], microalgae oil [21–24] and their mixtures with petroleum products [10,25]. Some studies were on hydrotreatment of FAME of vegetable oils [26,27] and one recent study was on the hydrodeoxygenation of palmitic acid as a model compound for microalgae oil [28].

In the present work, we have selected jatropha oil as a feed for the production of renewable diesel. Jatropha is an important non-edible feedstock for bio-fuel production. Jatropha plant is robust, drought-resistant, long-lasting and can be grown in infertile soil with little or no care. The gestation period of the jatropha plant is low and possible yield potential is very high (i.e. 3–5 kg of seeds per plant and 1–1.5 tonnes of oil per hectare) [29]. All these features of jatropha plant are favourable for the commercialization of this process. Desulfurization catalysts (CoMo, NiMo, NiW etc.) have been extensively used for hydrotreatment of jatropha oil [2,3,6]. These catalysts show very good activity towards the hydrotreatment process. But such catalysts are more active in their sulfided form. Due to this, prior to the reaction, these catalysts need to be activated by sulfidation. The sulfidation can be done by passing H_2S over the catalyst bed [2,3,6] or by adding sulphur-containing compounds (e.g., dimethyldisulphide) to the feed oil [13,18]. The drawbacks associated with the sulfidation process are: it releases H_2S to the atmosphere, which is harmful and traces of sulphur go to the product stream, which affects the quality of the product. However, noble metal catalysts show very good activity for hydrotreatment and they do not require pre-treatment by sulfidation. There are several comprehensive studies on hydrotreatment of vegetable oils over noble metal catalysts supported on various supports. For example, Kikhtyanin et al. reported the hydroconversion of sunflower oil over Pd/SAPO-31 catalyst [11]. Activity of zeolite supported Pt-Re catalyst towards hydrotreatment of jatropha oil was investigated by Murata et al. [5]. Lui et al. tested Ru/

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Al_{13}-Mont catalysts for the hydrotreatment of waste cooking oil [30]. Patel et al. studied the hydrotreatment of algae biocrude over γ-alumina supported Pt, Pd, Ru and NiMo catalysts [31]. Using Ru/$La(OH)_3$ catalyst, Guo et al. produced paraffin fractions from jatropha oil at mild reaction conditions [32].

Hydrotalcites are layered double hydroxides of divalent and trivalent cations (such as magnesium and aluminium) with exchangeable interlayer of carbonate ions and water molecules. By controlled thermal decomposition, layered double hydroxides can be converted into the mixed oxides with small crystal size and high specific surface area. Because of the presence of Mg, these mixed oxides are basic in nature [33]. In this process of hydrotreatment of vegetable oils, basic nature of catalyst support can improve the efficacy of the catalyst by facilitating the adsorption of the acidic intermediates (fatty acids) which are formed during the reaction [32]. Some of the earlier studied catalysts for hydrotreatment include mixed oxides from hydrotalcite as catalyst supports [34–37].

In this study, we have impregnated the noble metals (Pd and Ru) on lab-made HTlc and tested their activity towards hydrotreatment of jatropha oil to produce diesel-range hydrocarbons. The activity trials of both the catalysts were taken in a trickle-bed reactor over wide ranges of temperature (603–663 K), weight hourly space velocity (WHSV, 1–4 1/h) pressure (1.5–3 MPa) and H_2/oil ratio (200–1000 v/v). To the best of our knowledge, HTlc supported noble metal catalysts have not been tested for the hydrotreatment of vegetable oils.

2. Experimental

2.1. Materials

Commercially available jatropha oil (from SVM Agrochemicals Pvt. Ltd. Nagpur, India) was used as feedstock for this process. The hydrogen (H_2) gas cylinder (with 99% purity) was provided by Rakhangi Gas Suppliers, Mumbai. To identify and quantify the gaseous products, the standard mixture of gases containing H_2, N_2, CO, CH_4, CO_2, C_2H_6 and C_3H_8 were purchased from Chemtron Science Laboratories Pvt. Ltd. The precursors of palladium and ruthenium ($PdCl_2$ and $Ru(NO_3)_3$) respectively were purchased from Aldrich. Standards for fatty acid methyl esters and liquid hydrocarbons of diesel were purchased from Sigma Aldrich. The reagents like citric acid, phosphoric acid and sodium hydroxide used in the oil degumming process were purchased from S. D. Fine Chem. Ltd., Mumbai.

2.2. Jatropha oil characterization

The degumming of jatropha oil was carried out by water degumming, acid degumming and TOP degumming processes, which are described in the literature [38]. Key properties of jatropha oil such as saponification value, acid value, iodine value, density, cloud point, pour point and flash point were measured. The values of these properties were found to be: saponification value = 201 mg KOH/g, acid value = 7.5 mg KOH/g, iodine value = 100 g I_2/100 g oil, density = 0.94 g/cm^3, cloud point = 280 K, pour point = 275 K and flash point = 495 K. The elemental analysis of jatropha oil was carried out by Thermo Finnegan Analyser (Flash EA1112 series, Italy). The elemental composition of the oil is as follows: C = 77.03%, H = 9.8%, O = 10.54% and N = 1.72%. Vegetable oils differ in the fatty acid composition. Depending on the extent of unsaturation in the oil feedstock, the consumption of H_2 in the hydrotreating process varies. Thus, oils rich in unsaturated fatty acids require more H_2 than oils with less unsaturation. To find out the fatty acid composition of the jatropha oil, triglycerides of the oil were transformed into the fatty acid methyl esters (FAME) using methanol and sodium hydroxide. FAME was analysed by gas chromatography technique using FID detector and BPX-70 column (50 m × 0.2 mm × 0.25 μm). The oil was composed of 13.49% of palmitic acid, 1.09% of palmitoleic acid, 5.23% of stearic acid, 43.57% of oleic acid and 36.62% of linoleic acid.

2.3. Catalysts preparation and characterization

The HTlc was prepared by the co-precipitation method as described in the literature [33]. The nitrates of nickel, magnesium and aluminium were used as precursors. These salts were taken in the appropriate proportion to maintain the desired ratio of the Mg to Al (i.e. 3/1). An aqueous solution of precursor salts (nickel nitrate, magnesium nitrate and aluminium nitrate) was prepared and added to a beaker containing aqueous solution of sodium carbonate with continuous stirring. The pH of the solution was maintained at 10 using 2 M sodium hydroxide solution. The resulting suspension was then kept for aging for 24 h at room temperature. The obtained precipitate was filtered and washed with deionised water to remove nitrate ions and kept for drying overnight at 383 K. The precipitate was ground to fine particles and then calcined at 1073 K for 5 h in air. The material was crushed and sieved (mesh size: 30–60).

Mixed oxides obtained from calcinations of hydrotalcites were impregnated with aqueous solutions of palladium chloride and ruthenium chlorides as per wet impregnation procedure reported in the literature [39]. To achieve complete solubility of $PdCl_2$ in water, few drops of hydrochloric acid were added to the solution. Then resulting slurry was dried at 353 K for 24 h and finally calcined at 773 K for 5 h. Finally, the catalysts were crushed and sieved with mesh size 30–60 i.e. 0.3–0.6 mm. For both the catalysts, 2% of noble metal loading was chosen.

Calcined and non-reduced HTlc-supported Pd and Ru catalysts were characterized by different analytical techniques. Surface morphologies of the catalysts were studied by Field Emission Gun Scanning Electron Microscopy (FEG-SEM) technique using TESCAN MIRA 3 model with beam SE detector at 15 kV. Crystallinity and the distribution of crystallographic orientation of the catalysts were studied using X-ray diffraction (XRD) patterns, which were recorded using a Rigaku-Miniflex powder diffractometer with CuK (1.54 Å) radiation. Brunauer-Emmet-Teller (BET) surface area, pore volume and pore diameter of the catalyst were estimated by nitrogen adsorption-desorption method (Micromeritics ASP2010).

2.4. Experimental set up and procedure

A trickle-bed rector provided by Chemito Technologies Pvt. Ltd., Mumbai, was used to perform the hydrotreatment experiments. The tubular reactor was made up of SS316 material. The reactor dimensions were: length = 49 cm, outer diameter = 2.54 cm and inner diameter = 2.48 cm. The setup was provided with a feed vessel (FV), gas-liquid separator (GLS) and four electrically heating furnaces among which two were pre-heaters (PH1 and PH2) and two were furnaces to heat the reactor (FH1 and FH2). It also consisted of a high-pressure pump to feed the oil to the system and two mass flow controllers (MFC1, MFC2) to control the flow of N_2 and H_2 gases respectively. The required pressure of the system was maintained by a back-pressure regulator (BPR), which was placed between the tubular reactor and GLS. To monitor the reaction parameters, the reactor system was equipped with a PID controller as well as Proficy HMI/SCADA-iFIX software.

While performing hydrotreatment reactions to avoid channelling of oil, the catalyst was mixed with the quartz powder. This mixture was