Research Paper

Biodiesel production from used cooking oil using a novel surface functionalised TiO$_2$ nano-catalyst

Jabbar Gardy [a], Ali Hassanpour [a,*], Xiaojun Lai [a], Mukhtar H. Ahmed [b], Mohammad Rehan [c]

[a] School of Chemical and Process Engineering, University of Leeds, LS2 9JT Leeds, UK
[b] Nanotechnology Integrated Bioengineering Centre, University of Ulster, Jordanstown, BT37 0QB Belfast, UK
[c] Centre of Excellence in Environmental Studies (CEES), King Abdulaziz University, Jeddah, Saudi Arabia

ABSTRACT

A novel, efficient and recyclable mesoporous TiO$_2$/PrSO$_3$H solid acid nano-catalyst was synthesised by the post-synthetic grafting of propyl sulfonic acid groups onto a mixed phase of a TiO$_2$ support. The synthesised nano-catalyst was characterised using FTIR, SEM, TEM, XPS, N$_2$ adsorption–desorption isotherms, XRD, DSC, TGA, and CHNS analysis. The loading percentage of propyl sulfonic acid on the TiO$_2$ support was calculated using CHNS analysis and TGA. The catalytic performance of TiO$_2$/PrSO$_3$H on the production of the fatty acid methyl esters (FAME) via simultaneous esterification and transesterification reactions from used cooking oil (UCO) has been studied. The effects of different process parameters showed that 98.3% of FAME can be obtained after 9 h of reaction time with 1:15 molar ratio of oil to methanol, 60 °C reaction temperature and 4.5 wt% catalyst loading. It was also found that the one-pot post-surface functionalisation strategy with hydrophilic functional groups (–SO$_3$H) enhanced the acid strengths of the nano-catalyst providing more acid sites for the reactants, and improving the accessibility of methanol to the triglycerides (TG)/free fatty acids (FFAs) by increasing the pore volumes/sizes of the nano-catalyst. The solid acid nano-catalyst was re-used in four consecutive runs without significant loss of catalytic efficiency. Finally, the synthesised biodiesel fuel satisfied ASTM and EN standards.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Nanomaterials have fascinating and unique properties for the usage in various industrial fields. Titanium dioxide nanoparticles (TiO$_2$ NPs) are among the most widely studied for their use in photocatalysis, gas sensors, medicine, catalyst support, pigments, cosmetics and solar cells [1–3]. This is due mainly to their favourable properties, acidity, wide band gap, high surface area, low cost and high availability, better redox selectivity, good mechanical and chemical stability, high reactivity, low toxicity, and high reusability [4–6]. TiO$_2$ NPs naturally occur in three main crystallographic phases, these being anatase, rutile, and brookite [2], but the most commonly used, because of its highly photocatalytic activity properties, is a mixture of anatase and rutile phases of TiO$_2$ [7].

Because of their multiple potential applications, straightforward recoverability and excellent properties, a wide range of recent studies on synthetic routes have been undertaken to fabricate surface modified nanoparticles in order to increase their surface acidity/basicity [8–13]. This is of particular significance in relation to nano-catalysts for biodiesel production involving the use of cheap raw materials containing FFAs as the acid catalysts can facilitate simultaneous esterification of FFAs and transesterification of TG without soap formation [14,15]. In the context of green chemistry, recycled vegetable oils could be used as inexpensive feedstocks for biodiesel fuel production [16–18]. Such use helps to reduce environmental pollution and utilises economies for cheap biodiesel production [19–21]. The yield and quality of biodiesel can be highly affected by the surface area, surface acidity/basicity, and particle size of the catalysts used in the esterification and/or transesterification processes [22]. This has encouraged the development of novel recyclable solid acid nano-catalysts to replace conventional corrosive homogeneous acid catalysts [21,23], which can corrode reactors and requires further washing with neutralisation steps for their removal from the biodiesel and its by-products [24].

According to the literature, the surface modification of nanoparticles could create solid acid nano-catalysts [25]. The surface modification could be carried out through different strategies such as chemical treatments, ozonolysis, polymer grafting,

encapsulation in a silica shell (silanisation), ligand exchange technique, or capping agents (surfactants)/encapsulation in a surfactant corona [26,27]. Modification of the surface of nanoparticles by integration of acidic functional groups (e.g. $-SO_3H$) to produce solid acid catalysts for different applications has been highlighted in the literature over the recent years [8,11,21,24,28–38]. This is because sulfonic acid functional groups on the surface of nanoparticles lead to the formation of porous materials with high accessibility to the active sites [39].

There are several recent works describing the performance of such promising materials for the biodiesel production [10,19,31,40–42]. The surface modification of mesoporous materials, such as SBA-15, with organosilane sulfonic groups increases the hydrophobic character of the solid acid catalyst surface resulting in high catalytic activity and selectivity toward glycerol in the esterification of FFAs [43]. However, these types of catalysts are quite sensitive to the presence of impurities in raw materials such as recycled oil feedstocks [44]; also, low sulfonic acid sites loading on the surface of nanoparticles are hampered in practical application of such catalysts [37]. Furthermore, fast deactivation is another practical problem for such catalyst. Therefore, there is a need to synthesise stronger and more tolerant nano-catalysts with higher re-usability for cheap feedstocks such as used cooking oil (UCO).

There are, so far, no reports on the surface functionalisation of titania with 1,3-propyl sultone for a direct-preparation of propylsulfonic acid grafting the surface of TiO_2 NPs and/or on the use of such material as a solid acid nano-catalyst for biodiesel production. Therefore, the present work describes the fabrication, characterisation and application of a novel TiO_2/propylsulfonic acid nano-catalyst in order to understand the impact of catalytic activity and reusability of such nano-catalyst on biodiesel production from UCO as a cheap feedstock. Finally, the synthesised biodiesel from the catalytic esterification/transesterification processes was analysed in accordance to ASTM and EN standard methods.

2. Experimental

2.1. Materials and methods

2.1.1. Synthesis of solid acid nano-catalysts

The surface charge of titania NPs is pH dependent. Therefore, we pre-treated the titania NPs with aqueous solution of ammonium hydroxide to reduce the agglomeration and increase the receptor sites ($TiO_2 + nOH^- \rightarrow TiO_2(OH)n^{n-}$) on the surface of titania support [45]. 6 g of TiO_2 NPs (Sigma-Aldrich) was added slowly into a 50 ml of 0.5 M ammonium hydroxide solution (Sigma-Aldrich) at room temperature. The suspension was then sonicated for 30 min. The resultant was transferred into a centrifuge tube for washing with double deionised water and dried at 80 °C for 4 h in an oven. Typically, 1 g of the dried powder was charged into a three necked glass flask at ambient temperature then 20 ml suspension solutions of 0.1 molar 1,3-propane sulfone (Sigma-Aldrich) in dry toluene (Sigma-Aldrich) was added dropwise. The resultant suspension was slowly stirred under reflux for 72 h at 120 °C. The synthesised TiO_2/propyl sulfonic acid powders were cooled to room temperature. Thereafter the synthesised nano-catalyst was separated from the solution using a centrifuge and washed off several times with fresh toluene to remove the remained unreacted 1,3-propane sulfone. The resulting precipitate sample was dried overnight at 80 °C then denoted as $TiO_2/PrSO_3H$.

2.1.2. Synthesis of biodiesel fuel

The simultaneous esterification and transesterification of UCO was performed in a glass batch reactor connected with an automatic temperature controller loop system under constant agitation rate at 600 RPM using a digital mechanical stirrer and a reflux condenser. The sample of UCO obtained from a local restaurant in Leeds, UK, was pre-treated by filtration process to remove solid impurities and heated to 100 °C for a few hours to remove the moistures. Specified amounts of pre-treated UCO, $TiO_2/PrSO_3H$ nano-catalyst and methanol (Sigma-Aldrich) were charged into the batch reactor. The three-phase (solid–liquid–liquid) mixture was mixed at 600 RPM and heated to specified temperatures and times. The final reaction mixture was transferred into a separating funnel and allowed to cool to room temperature. A few millilitres of aliquot was withdrawn from the upper layer, biodiesel phase, and separated from the remaining impurities using a centrifuge at 9000 RPM for 10 min to quantify the fatty acid methyl ester (FAME) content of the samples by off-line gas chromatography (GC) [4].

2.2. Characterisation methods

2.2.1. Catalyst characterisation

Physicochemical properties of the prepared $TiO_2/PrSO_3H$ and TiO_2 nano-catalysts were fully characterised as follows: Fourier transform infrared (FT-IR) spectroscopy was measured at room temperature using a Nicolet iS10 FT-IR spectrometer fitted with a DTGS-KBr detector. A minimum of 36 scans were performed at the average signal of infrared with a resolution 4 cm^{-1} in the ranges of 500 to 4000 cm^{-1}. Particle size and surface morphologies were observed with a high performance cold field emission scanning electron microscopy (CFE-SEM, SU8230 Hitachi) and transmission electron microscopy (TEM, FEI Titan Themis Cubed 300). The location of the elements and elemental compositions of the prepared nano-catalyst sample were identified using the TEM fitted with high-angle annular dark field (HAADF) detector operated at an accelerating voltage of 300 kV equipped with an energy dispersive X-ray spectroscopy (EDS, Oxford INCA 350). Nitrogen porosimetry was obtained at −196 °C on a Micromeritics TriStar 3000 surface analyser. Prior to the measurements, the nano-catalyst sample was degassed in a vacuum oven overnight at 120 °C. The X-ray photoelectron spectroscopy (XPS) was performed using a KRATOS XSAM 800 equipped with an energy analyser and monochromated Al-Kα X-ray source (hv1486eV) generated from aluminium anode. The film of the nano-catalyst sample was prepared by dissolving a few milligrams of catalyst sample in chloroform and methanol (3:1) then coating on the silicon wafer surface. CasaXPS version 2.3.17 was used for spectral fitting and binding energies corrected to the C 1s peak at 285 eV to compensate for residual charging effects. The bulk and surface sulfonic acid loadings on the surface of the nano-catalysts were determined via elemental analysis (Thermo Scientific™ FLASH 2000 CHNS Analyser) and XPS, respectively. The thermal stability was carried out on a Mettler Toledo (TGA/DSC-1) star^e system. The system was programmed to heat up from 25 to 900 °C at 10 °C/min under nitrogen gas at 50 ml/min with a constant flow rate. Total propyl sulfonic acid loadings were calculated from the TGA weight loss between 200 and 600 °C. XRD patterns were recorded on a Bruker D8 X-ray diffraction, fitted with a Cu K_α radiation (1.54 Å, 40 kV, 40 mA). Data was collected from 2θ angle ranging of 10– 70° with step size 0.0495° at 35 s per step.

2.2.2. Biodiesel characterisation

The flash point of prepared biodiesel sample was measured by an auto ramp closed cup flash point tester (Setaflash series 3, England) equipped with a coolant block unit. The temperature ramped at 1–2 °C/min until the flash was captured. Moreover, the pycnometric method was used to determine the density of obtained biodiesel at 15 °C. Furthermore, viscosity of prepared biodiesel was measured on a Bohlin-Gemini 150 rotary rheometer (Malvern, UK). Additionally, trace moisture content in biodiesel was analysed by volumetric Karl Fischer titration (Mettler Toledo-V20, Germany).