Journal of Molecular Catalysis A: Chemical 411 (2016) 110–116

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Sulfonated porous organic polymer as a highly efficient catalyst for the synthesis of biodiesel at room temperature

Ruth Gomes, Piyali Bhanja, Asim Bhaumik*

Department of Material Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

ARTICLE INFO

Article history:
Received 12 August 2015
Received in revised form 9 October 2015
Accepted 13 October 2015
Available online 23 October 2015

Keywords:
Porous organic polymer
Sufonic acid functionalization
High surface acidity
Biodiesel synthesis

ABSTRACT

A new functionalized porous organic polymer bearing sulfonic acid groups (PDVTA-SO_3H) at the pore surface with high surface area ($S_{BET} = 406\,m^2\,g^{-1}$) and Brønsted acidity is reported. The material has been synthesized via post-synthetic sulfonation of the porous co-polymer poly-divinylbenzene-*co*-triallylamine (PDVTA-1) using chlorosulfonic acid as sulfonating agent. A detailed characterization of the —SO_3H functionalized porous polymeric material has been carried out using N_2 sorption, FT-IR and UV–vis spectroscopy, HR-TEM, FE-SEM, thermogravimetric and elemental analyses. Temperature programmed desorption of NH_3 (TPD-NH_3 analysis) of PDVTA-SO_3H revealed a very high surface acidity of 2.3 mmol g^{-1}. Such high acidity of PDVTA-SO_3H has been explored to investigate its catalytic efficiency towards eco-friendly production of biodiesel via esterification of long-chain free fatty acids (FFA) to the respective fatty acid monoalkyl esters (FAMEs) at room temperature using methanol as reactant as well as solvent. The sulfonated porous polymer is found to be a very active and reusable solid acid catalyst giving high yields (~92–98%) of various biodiesel compounds under very mild reaction conditions.

1. Introduction

Synthesis of biofuel compounds i.e. fatty acid monoalkyl esters (FAMEs) are of huge demand as they provide renewable, non-toxic and eco-friendly source of energy and a possible replacement of fossil fuels [1]. Large scale use of the fossil fuels with the advancement of today's world would cause severe energy crisis in future due to its limited reserves, emission of greenhouse gases and environmental pollution caused during their ignition. Biofuel compounds can overcome such problems as they are renewable and can be produced from low cost resources such as animal fat and vegetable oil containing free fatty acids (FFA) [2–6]. The biodiesel compounds can be synthesized by esterification of long chain fatty acids with aliphatic alcohols. However, the commercial production of biodiesel is associated with major problems of high production cost, product isolation, catalyst separation etc. as the synthesis involves homogeneous strong acid or base catalyzed esterification of fatty acids. The conventional use of concentrated sulfuric acid as homogeneous acid catalyst is not very favorable due to its corrosive nature. Although the base catalyzed synthesis of biodiesel via transesterification reaction occurs at low temperature and lesser reaction time but the process requires a pre-esterification step to prevent saponification between the FFAs and base. This is because of the fact that low-cost feedstock containing high FFA causes saponification under basic condition, which leads to a major problem in product separation and the process consumes large excess of catalyst. Thus, a wide scale research focusing on the design of suitable heterogeneous solid acid catalysts has been undertaken [7,8]. Several solid acids have been reported till date to catalyze the esterification reaction, such as transition metal oxides [9–11], Au NP/nanoporous polymer [12], ion exchange resins [13], molecular sieves [14], functionalized silica [15], zeolites [16], metallo phosphates [17,18], metal organic framework [19], functionalized porous carbons [20,21] and mesoporous silica materials [22–24]. But for most of these cases the reaction needs high temperature and pressure due to low concentrations of the catalytically active sites.

On the other hand, porous organic polymers bearing suitable functional groups at the pore surface are very demanding. These materials are potential candidates for a wide range of application areas such as gas adsorption [25–27], catalysis of various important organic transformations [28–34], drug delivery vehicle [35], sensing [35,36] and so on. Due to high specific surface area and pore volume the target molecule can interact more easily with the required functional group present at the surface compared to non-porous materials. Intense research has being carried out on

---

* Corresponding author.
E-mail addresses: msab@iacs.res.in, abhaumik68@yahoo.co.in (A. Bhaumik).

http://dx.doi.org/10.1016/j.molcata.2015.10.016
1381-1169/

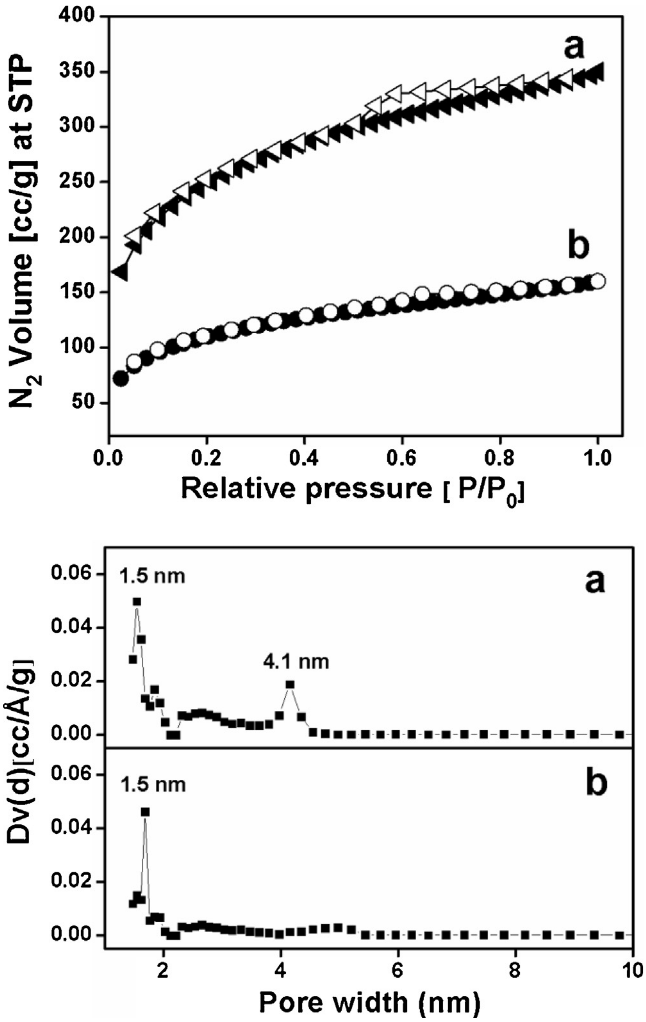


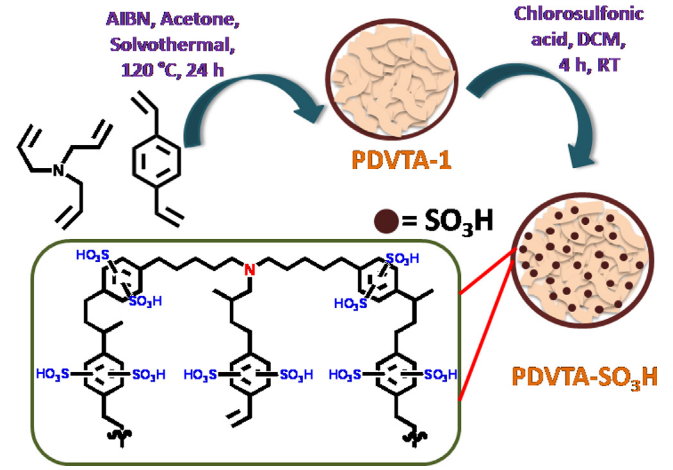
Fig. 1. Above N_2 adsorption (filled)–desorption (empty) isotherms of (a) PDVTA-1 and (b) PDVTA-SO_3H at 77 K. Below their pore size distribution using the Non Local Density Functional Theory (NLDFT) Model is shown respectively.

the designing of appropriate porous organic polymers for catalytic applications. Porous polymers rich in acidic functionality are thus highly demanding for the synthesis of biodiesels via esterification/transesterification reactions. In our present work, we report the synthesis of a new solid acid catalyst containing —SO_3H group in the porous organic polymer network with high surface acidity for the synthesis of biodiesel products. The catalyst is thoroughly characterized using various instrumental techniques to investigate its BET surface area/porosity, framework-bondings, chemical environment, thermal stability and surface acidity. Various long chain fatty acids are used for the catalytic reactions and we have measured the recycling efficiency of the catalyst.

2. Experimental

2.1. Materials

Divinylbenzene (DVB, monomer) and triallylamine (TAA, monomer) were obtained from Sigma–Aldrich. Azobisisobutyronitrile (AIBN, radical initiator) was obtained from SRL and recrystallized from hot ethanol prior to use. Chlorosulfonic acid was purchased from Spectrochem, India. All other chemicals used in the experiments were of analytical grade produced by E-Merk.



Scheme 1. Schematic representation of the synthesis of sulfonated porous organic co-polymer PDVTA-SO_3H.

2.2. Instrumentation

A PerkinElmer Spectrum 100 was used to record the FT IR spectra of the PDVTA-1 and PDVTA-SO_3H. A UV 2401PC with an integrating sphere attachment was used to obtain UV–vis diffuse reflectance spectra of the materials using $BaSO_4$ as the background standard. N_2 adsorption/desorption isotherms of the porous organic polymers before and after sulfonation was recorded in a Quantachrome Autosorb 1-C at 77 K. The samples were degassed at 373 K for 8 h under high vacuum conditions prior to the measurement. High resolution transition electron microscopic (HR TEM) images of the catalyst were recorded using a JEOL 2010 TEM operated at 200 kV. Morphology and particle size of the sample was analyzed by using a Jeol JEM 6700 field emission scanning electron microscope (FE SEM). Elemental analyses of the materials were carried out using a PerkinElmer 2400 Series II CHN analyzer. Thermogravimetric analysis (TGA and DTA) of the catalyst was carried out between the temperature ranges from 308 to 873 K in a thermal analyzer TA-SDT Q-600 under N_2 flow. The temperature programmed desorption (TPD) of ammonia of the catalyst was recorded using a thermal conductivity detector (TCD) in a Micromeritics Chemisorb 2720 instrument. For the experiment, the material was first degassed in flow of He at a flow rate of 30 mL/min for 2 h at 373 K followed by saturating it with 10% NH_3 in He at room temperature for 30 min. Then the excess NH_3 was removed by flow of He (flow rate 30 mL/min) for 45 min and the desorption pattern of ammonia (carrier gas He) was studied by heating the sample from room temperature to 673 K at a temperature ramp of 10 °C/min. The ^1H and ^{13}C NMR spectra of the biodiesel compounds were recorded in a Bruker Advance 500 MHz NMR spectrometer.

2.3. Synthesis of the catalyst PDVTA-SO_3H

The porous organic polymer PDVTA-1 was synthesized as described before [37] through solvothermal co-polymerization of divinylbenzene and triallylamine by using AIBN as a radical polymerization initiator. For a typical synthesis of PDVTA-1, 521 mg divinylbenzene (4 mmol) and 137 mg triallylamine (1.0 mmol) were taken in a 50 mL round bottom flask. Then 10 mL dry acetone was added and the mixture was continuously stirred for 10 min under inert atmosphere. 25 mg AIBN (0.15 mmol) was then added to the mixture and resulting slurry was stirred for 3 h at room temperature. Finally the resultant mixture was autoclaved at 393 K for 24 h under static conditions. The final product was washed thoroughly with acetone and dried at 373 K. For the sulfonation step,