



## Esterification of free fatty acids for biodiesel production over heteropoly tungstate supported on niobia catalysts

K. Srilatha<sup>a</sup>, N. Lingaiah<sup>a,\*</sup>, B.L.A. Prabhavathi Devi<sup>b</sup>, R.B.N. Prasad<sup>b</sup>, S. Venkateswar<sup>c</sup>, P.S. Sai Prasad<sup>a,\*</sup>

<sup>a</sup> Catalysis Laboratory, I&PC Division, Indian Institute of Chemical Technology, Tarnaka, Uppal Road, Hyderabad 500607, A.P., India

<sup>b</sup> Lipid Science and Technology Division, Indian Institute of Chemical Technology, Hyderabad 500607, India

<sup>c</sup> University College of Technology, Osmania University, Hyderabad 500607, India

### ARTICLE INFO

#### Article history:

Received 6 February 2009

Received in revised form 5 May 2009

Accepted 12 May 2009

Available online 20 May 2009

#### Keywords:

Esterification

Sunflower oil free fatty acids

Palmitic acid

Methanol

Tungstophosphoric acid

Niobia

### ABSTRACT

A series of catalysts containing 5–30 wt% of 12-tungstophosphoric acid (TPA) supported on niobia were prepared and their catalytic activity was evaluated for esterification of free fatty acids with methanol. The catalysts were characterized by FT-infrared spectroscopy, X-ray diffraction and temperature programmed desorption of ammonia. The esterification activity depends on the content of TPA on niobia; the catalyst with 25 wt% of TPA exhibited highest activity. The best catalyst was subjected to different calcination temperatures to study the structural changes. We observed that esterification activity depends upon the structural variations of the catalyst. The effects of reaction variables such as catalyst loading, methanol to acid ratio, reaction time and temperature on the conversion of fatty acid were studied. The esterification activity of the catalysts is correlated with the characteristics of the catalysts.

© 2009 Published by Elsevier B.V.

### 1. Introduction

Depletion of the world petroleum reserves and increasing environmental concerns has stimulated the search for renewable fuels. Biodiesel is receiving increased attention as an alternative, non-toxic and biodegradable renewable fuel [1]. However, biodiesel is currently not cost competitive with conventional diesel fuel because of its high raw material and production costs. To improve biodiesel economics, feedstock selection becomes critical. The biodiesel feeds containing high free fatty acid (FFA) are cheaper than oils without FFA. Unfortunately, utilization of high FFA acid feeds in traditional biodiesel production processes leads to depletion of the catalysts as well as increased purification costs, since the free fatty acid is saponified by the homogeneous alkaline catalyst, producing excess soap [2].

This problem can be circumvented by an esterification pretreatment of the free fatty acids to alkyl esters in the presence of an acidic catalyst. Then triglycerides can be processed under standard transesterification reaction conditions [3]. Usually, esterification is carried out using various conventional mineral acids such as H<sub>2</sub>SO<sub>4</sub>, HF, H<sub>3</sub>PO<sub>4</sub> and HCl. The replacement of these

hazardous and polluting corrosive liquid acids by solid acid catalysts is one of the major demands of society. There are few reports about the esterification of free fatty acids in the biodiesel production. Mesoporous materials [4], anionic resins [5], supported Nafion<sup>®</sup> resin [6] and supported materials like WO<sub>3</sub>/ZrO<sub>2</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub> [7,8] all showed activity for the esterification of different fatty acids. Most of these catalysts are studied for esterification of individual acids. In certain cases, the esterification of free fatty acids of vegetable oils are also studied. However, these solid acid catalysts are active only at high temperatures.

Heteropoly acids (HPAs) are typical strong Bronsted acids and catalyze a wide variety of reactions in both homogeneous and heterogeneous phases, offering more efficient and cleaner processes [9–12]. The major disadvantages of HPAs as catalysts lie in their low thermal stability, low surface area (1–10 m<sup>2</sup>/g) and solubility in polar media. HPAs can be made ecofriendly insoluble solid acid catalysts with high thermal stability and surface area by supporting them on suitable supports. The support provides an opportunity to HPAs to be dispersed over a large surface area, which increases the catalytic activity. Various supports like silica [9,10], titania [11,12], active carbon [13–15], MCM-41 [16–18], acidic ion exchange resins [19] and clays [20–22] have been used as supporting materials.

Niobium is known as an interesting and important catalyst as well as a support for different catalytic reactions. The catalytic applications of niobium compounds have increased in recent years

\* Corresponding authors. Tel.: +91 40 27193163; fax: +91 40 27160921.

E-mail addresses: [nakkalingaiah@iict.res.in](mailto:nakkalingaiah@iict.res.in) (N. Lingaiah), [saiprasad@iict.res.in](mailto:saiprasad@iict.res.in) (P.S. Sai Prasad).

[23]. Niobia can also be used as a promoter and also as a solid acid catalyst. Since it is reducible over a wide temperature range, niobia is also known as a typical strong metal support interacting with (SMSI) oxide [24].

In the present study, 12-tungstophosphoric acid supported on niobia catalysts are studied for the esterification of free fatty acids. Palmitic acid (C16 acid) and mixture of FFA of sunflower oil (SFFA) have been selected for testing the esterification efficiency of the catalysts. An effort has been made in the present investigation to understand the nature of the active species formed on the support and the variations with TPA content and calcination temperature.

## 2. Experimental

### 2.1. Preparation of catalyst

The niobium oxide used to impregnate heteropoly tungstate was prepared by calcination of niobic acid (CBMM, Brazil) in air at 500 °C for 4 h. A series of catalysts with TPA loadings ranging from 5 to 30 wt% supported on niobium oxide was prepared by an impregnation method. Required amounts of TPA dissolved in minimum amounts of water were added to the support and the catalyst masses were allowed to equilibrate for 2 h. Later the excess water was removed on a water bath. The catalyst masses thus obtained were further dried at 120 °C for 12 h and subsequently calcined at the desired temperature for 2 h.

### 2.2. Characterization of samples

X-ray diffraction (XRD) patterns of the powdered samples were recorded on a Siemens D-5000 diffractometer using nickel-filtered  $\text{CuK}\alpha$  radiation. The intensity data were collected over a  $2\theta$  range of 10–80°. The FT-IR spectra were recorded on a Biorad Excalibur spectrometer using the KBr disc method. Temperature programmed desorption of ammonia (TPDA) was carried out on a laboratory-built apparatus equipped with a gas chromatograph using a TCD detector. In a typical experiment, about 0.1 g of the oven dried sample was taken in a quartz tube. Prior to TPD studies, the catalyst sample was treated at 300 °C for 1 h by passing pure helium (99.9%, 50 ml/min). After pretreatment, the sample was saturated with anhydrous ammonia (10%  $\text{NH}_3$ –90% He mixture gas) at 100 °C at a flow rate of 50 ml/min for 1 h and was subsequently flushed with He at the same temperature to remove physisorbed ammonia. The process was continued until a stabilized base line was obtained in the gas chromatograph. Then the TPDA analysis was carried out from ambient temperature to 800 °C at a heating rate of 15 °C/min. The amount of  $\text{NH}_3$  evolved was calculated from the peak area of the already calibrated TCD signal.

### 2.3. Catalytic reaction

The esterification of palmitic acid/FFA of sunflower oil was carried out in liquid phase at atmospheric pressure in the reaction temperature range of 35–65 °C. The experiments were carried out on a Radleys parallel synthesizer, which contains six 250 ml round bottom flasks. The synthesizer had the provisions for stirring, refluxing and measuring the reaction temperature. In a typical experiment, 2 g of free fatty acid was taken in the round bottom flask and 60 ml of dry methanol was added. About 10% of solid acid catalyst was taken and the reaction mixture was refluxed with constant stirring. After completion of the reaction or after attaining the desired reaction time, the catalyst was separated by filtration. The methanol present in the filtrate was removed on a Rota evaporator. The conversion of free fatty acid into ester was estimated by measuring the acid value of the product.

## 3. Results and discussion

### 3.1. Characterization of the catalysts

The XRD patterns of the catalysts along with that of the support niobia are shown in Fig. 1. The patterns show predominantly peaks related to the support. There are no diffraction patterns of TPA for the catalysts with low TPA (5–15%) loading, indicating that it is in well-dispersed state. Similar observations are reported for the supported catalysts with low amount of heteropoly acid [25]. The peaks related to TPA are present in catalysts with high TPA loading (20–30 wt %). Pure  $\text{Nb}_2\text{O}_5$  shows the lines pertaining to hexagonal phase (TT Phase according to Schaffer notation). This is in agreement with the structure of  $\text{Nb}_2\text{O}_5$  reported by Ko and Weissman [26]. The XRD results corroborate the presence of Keggin ions of TPA on niobia.

FT-IR is a promising technique for the elucidation of structures of the heteropoly tungstates. The FT-IR spectra of the catalysts are presented in Fig. 2. The intensities of the bands related to Keggin ions are clearly seen for the catalysts with high TPA content. The bands that appear at 1081, 981, 887 and 799  $\text{cm}^{-1}$  are related to stretching vibrations of P–O<sub>a</sub> (O<sub>a</sub> – oxygen atoms bound to three W atoms and to P), W–O<sub>t</sub> (O<sub>t</sub> – terminal oxygen atom), W–O<sub>b</sub>–W (O<sub>b</sub> – corner sharing bridging oxygen atom) and W–O<sub>c</sub>–W (O<sub>c</sub> – edge sharing bridging oxygen atom), respectively [27]. The FT-IR data imply the retention of Keggin structure during the impregnation of TPA on niobia.

Ammonia adsorption–desorption technique usually enables the determination of the strength of acid sites present on the catalyst surface together with the total acidity. The  $\text{NH}_3$ -TPD profiles of the samples are shown in Fig. 3. The acid strength distribution calculated based on the  $\text{NH}_3$ -TPD are presented in Table 1. The support showed a broad desorption peak in between 180 and 280 °C. This broad low temperature peak indicates the moderate acidity of the support. The peaks are not well resolved for the catalysts with low TPA content. However, at higher TPA content the catalysts exhibited distinct desorption peaks. The samples with high TPA loading showed a low temperature desorption peak around 250–300 °C and two high temperature peaks in the range of 560–680 °C. The low temperature broad desorption peak originates from the acidity of the support. The intensity of the high temperature desorption peak is seen to be increasing as the TPA content increased. The desorption peaks at high temperature could be related to the strong acidic sites generated due to the presence

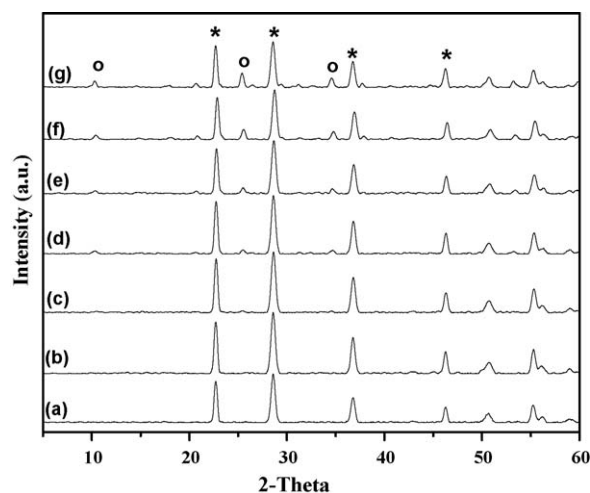


Fig. 1. XRD patterns of (a)  $\text{Nb}_2\text{O}_5$ , (b) 5% TPA/ $\text{Nb}_2\text{O}_5$ , (c) 10% TPA/ $\text{Nb}_2\text{O}_5$ , (d) 15% TPA/ $\text{Nb}_2\text{O}_5$ , (e) 20% TPA/ $\text{Nb}_2\text{O}_5$ , (f) 25% TPA/ $\text{Nb}_2\text{O}_5$  and (g) 30% TPA/ $\text{Nb}_2\text{O}_5$ . Catalysts: (O) TPA and (\*) hexagonal  $\text{Nb}_2\text{O}_5$ .

Download English Version:

<https://daneshyari.com/en/article/42603>

Download Persian Version:

<https://daneshyari.com/article/42603>

[Daneshyari.com](https://daneshyari.com)