Direct synthesis of mesoporous 12-tungstophosphoric acid SBA-15 catalyst for selective esterification of glycerol and lauric acid to monolaurate

Peng-Yong Hoo, Ahmad Zuhairi Abdullah *

School of Chemical Engineering, Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia

HIGHLIGHTS

- Direct synthesis method of 12-tungstophosphoric acid SBA-15 catalyst.
- Surface characteristics retention at anions concentration below 20 wt.%.
- Formation of tungsten oxides at anions concentration above 20 wt.%.
- Direct esterification of glycerol with lauric acid to monolaurate.
- Elucidation of effects of process variables.

GRAPHICAL ABSTRACT
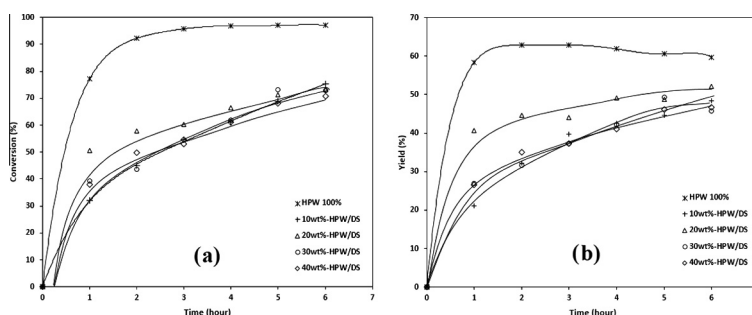
ABSTRACT

Via direct synthesis method, highly uniformed SBA-15 catalysts functionalized with 12-tungstophosphorus acid (HPW) were synthesized. Their characteristics were investigated using BET surface analysis, NH_3-TPD, FTIR, SEM, TEM, EDS and TGA. Surface defects were found in catalysts with high HPW loading (30–40 wt.%). High loadings also caused the deposition of HPW on the external surface and subject to oxidative decomposition to WO_3 that affected their acidity. HPW in mesopores had better thermal stability. High lauric acid conversion (70%) and monolaurin yield (50%) were shown in 6 h at 160 °C by the catalyst with 20 wt.% HPW. Lower yield was achieved at higher temperature. Its ordered mesoporosity evidently resulted in shape selectivity effect to suppress by-products formation. Effects of reaction temperature (150–170 °C), reactant ratios (1:1–5:1) and catalysts loadings (1–5 wt.%) were thoroughly elucidated.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Glycerol is produced as a by-product from oleochemical, soap making and biodiesel industries [1,2]. Its oversupply worldwide nowadays has affected its supply-demand relationship and by producing more value-added chemicals from it, more demand for this substance could be created [2]. Generally, monoglyceride can be synthesized using direct esterification of glycerol with fatty acid in the presence of acidic catalyst at low temperature (363–393 K) [3]. Traditionally, sulfuric acid, phosphoric acid and organic sulfonic acid are used in the process [2]. The products mixtures usually contain 40–60% of monoglyceride, 35–45% of diglyceride and triglyceride, some salts and other by-products together with the homogeneous catalysts used [4]. Therefore, further expensive product purification processes such as molecular distillation, neutralization and discoloration are generally needed [4]. Another issue in this reaction is to achieve high selectivity to monoglycerides at high conversion as deep esterification reactions usually occur. Thus, heterogeneous catalysts that can show shape selectivity effect need to be designed.

* Corresponding author. Tel.: +60 4 599 6411; fax: +60 4 5941013.
  E-mail address: chzuhairi@usm.my (A.Z. Abdullah).

Attempts to use catalysts based on acidic resin [5,6], zeolites [7], clay [8] and ordered mesoporous material [9] have been made. For the acidic active component of the catalyst, Keggin-type heteropoly acids (HPA) e.g. 12-tungstophosporic acid (HPW, $H_3PW_{12}O_{40}$) is one of the potential materials with significantly higher Brønsted acidity compared to mineral acid catalysts [10]. Meanwhile, SBA-15 support generally shows highly ordered hexagonal mesophase, high hydrothermal stability, high surface area (800 m^2/g) and average mesopores size (60 Å) [11]. It also has long mesopores with the width to length aspect ratio of 1:1000 that could provide high surface area within the mesopores that is particularly useful in many acid catalyzed reactions [12].

HPW have been introduced into SBA-15 and used for bifunctional conversion of *n*-decane [13]. The directly synthesized 30 wt.% HPW-SBA-15 catalyst showed 85.1% conversion and >70% yield. Different HPAs such as tungstophosphoric acid (PW), molydophosphoric acid (PMo) and tungstosilicic acid (SiW) have also been incorporated into SBA-15. Tropecelo et al. [14] found that the HPW incorporated SBA-15 was the best catalyst with 96% conversion in palmitic acid esterification with methanol. Brahmkhatri and Patel [15] investigated the potential of similar catalyst in biodiesel production. It consistently showed over 90% conversion as well as high reusability potential. However, reports on the use of this type of catalyst in glycerol esterification reactions are hardly found in literature. On top of that, several modifications of similar catalyst have been attempted to address and evaluate the leaching problem of such catalysts [16,17].

In this study, the behavior of HPW incorporated SBA-15 in glycerol esterification with lauric acid to selectively form glycerol monolaurate has been attempted. Particular focus has been given to shape selectivity effect in this catalyst. Correlations between catalyst characteristics and the catalytic behaviors have been established. In addition, effects of process variables such as HPW loadings, reaction temperature and reactant ratio have also been characterized.

2. Experimental

2.1. Synthesis of catalysts

HPW was incorporated into SBA-15 through a direct synthesis method outlined by Gagea et al. [13]. 1.92 g of Pluronic P123 (Sigma–Aldrich, Germany) was dissolved in 40 g of deionized water and 30 g of 4 M of HCl (R & J Chemicals) under stirring at 35 °C. The mixture was then heated up to 60 °C and added with appropriate amounts of HPW solution. The HPW solution was prepared beforehand with the desired amount of HPW dissolved in 5 g of deionized water. The HPW solution was then added into the polymer mixture drop-wise under vigorous stirring.

The mixture was kept under stirring at 60 °C for another 24 h. Then, 4 g of tetraethyl orthosilane (TEOS, Alfa Aesar) was added into the mixture under rapid stirring for 30 min. The formation of white precipitate could be immediately observed and the mixture was then transferred into a PE bottle and subjected to an aging process for 24 h at 80 °C under static condition. The solution was then removed from the bottle, washed with deionized water and filtered. The filtered white solid was then dried in an oven at 60 °C for 12 h followed by at 100 °C for another 12 h. The dried powder was then sent for calcination in a furnace at a ramping rate of 2 °C/min from room temperature to 300 °C and maintained there for 30 min, followed by 500 °C for another 6 h in air. The catalysts are denoted as *M* wt.%-HPW/DS in which the value of *M* could be 10, 20, 30 and 40.

2.2. Characterization of the catalysts

By using a Quanta-chrome Autosorb 1C surface analyzer operated at liquid nitrogen temperature, surface analysis of all synthesized catalysts were performed. Temperature programmed desorption of ammonia (NH_3-TPD) by means of Micromeritics Autochem II system allowed characterization of acidity in the catalysts. Meanwhile, the detection of specific chemical bonds within the catalysts was achieved by mean of a Shimadzu IRPrestige-21 Fourier-transformed infrared (FTIR) system.

For surface morphology analysis, a Quanta™ FEG 450 scanning electron microscope (SEM) system operated at 5.00 kV was used while the surface elemental analysis (EDS) was done using an Oxford Silicone Drift Detector (SDD) X-Max. Besides that, Philips CM12 transmission electron microscope (TEM) with Docu Version 3.2 image analysis enabled the characterization of mesoporous channels in the catalysts. Lastly, thermal gravimetric analysis (TGA) was achieved by means of an STA 6000 from Perkin–Elmer, USA.

2.3. Catalytic activity study

All the catalysts synthesized were tested for selective esterification of glycerol (R & J Chemicals) with lauric acid (R & J Chemicals) to selectively form glycerol monolaurin. The reaction was carried out in a batch system that consisted of a heating mantle with stirring and a three-necked flask as the reaction vessel. One of the necks was connected to a vacuum pump and another neck was dedicated to a thermocouple for temperature measurement. After the reaction, the product mixtures were analyzed using a gas chromatograph (Agilent Technologies 7890A GC system) equipped with a CP-Sil 5CB (15 m × 0.32 mm × 0.1 mm) column. The lauric acid conversion and monolaurin selectivity were calculated based on calculation methods proposed by Hermida et al. [18].

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. Surface analysis

All catalysts synthesized using direct synthesis method had high total surface area i.e. in the range of 169–521 m^2/g (Table 1). The surface area was found to decrease with increasing HPW loading. Thus, the introduction of HPW anions into the silica matrix would significantly change the surface characteristics. In this case, when more HPW anions were introduced, more deposition especially on the external surface occurred. Thus, a reduction in the surface area resulted [13]. On top of that, it is seen from SEM images that at higher HPW loading (40 wt.%), agglomeration of HPW crystal and tungsten oxide formed on the surface could drastically decrease the total surface area due to partial pore blockage.

Though the total surface area of all catalysts in this study decreased with higher HPW loading, the micropores and mesopores surface area did not always follow the same trend. Both microporosity and mesoporosity of these catalysts showed a non-systematic trend especially for 20 wt.%-HPW/DS. Interestingly, a drastic drop in total surface area of 20 wt.%-HPW/DS was observed, with much higher micropores area and lower mesopores area as compared with 30 wt.%-HPW/DS. These observations suggested that some abnormalities occurred in the pores that formed. On top of that, all catalysts showed reductions in both micropores and mesopores areas. Such phenomenon can be explained as more HPW anions being introduced into the silica support, the deposition of HPW on pores surface would reduce the pore size. Thus, an increase in microporosity could be observed with higher HPW