



## Research article

# Catalytic hydrogenation of soybean oil-derived fatty acid methyl esters over Pd supported on Zr-SBA-15 with various Zr loading levels for enhanced oxidative stability

Chachchaya Thunyaratchatanon<sup>a,b</sup>, Apanee Luengnaruemitchai<sup>a,b,c,\*</sup>, Nuwong Chollacoop<sup>d</sup>, Shih-Yuan Chen<sup>e</sup>, Yuji Yoshimura<sup>d,e</sup>

<sup>a</sup> The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Rd., Pathumwan, Bangkok 10330, Thailand

<sup>b</sup> Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University Research Building, Soi Chula 12, Phayathai Rd., Bangkok 10330, Thailand

<sup>c</sup> Center of Excellence on Catalysis for Bioenergy and Renewable Chemicals (CBRC), Chulalongkorn University, Phayathai Rd., Pathumwan, Bangkok 10330, Thailand

<sup>d</sup> Renewable Energy Laboratory, National Metal and Materials Technology Center (MTEC), 114 Thailand Science Park, Paholyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand

<sup>e</sup> Energy Catalyst Technology Group, Research Institute of Energy Frontier (RIEF), National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba 305–8569, Japan

## ARTICLE INFO

## Keywords:

Biodiesel  
Partial hydrogenation  
Oxidative stability  
Pd catalyst  
Zr-SBA-15  
XPS

## ABSTRACT

Partial hydrogenation of soybean oil (SO)-derived biodiesel, as fatty acid methyl esters (FAMES), over mesoporous palladium (Pd)/SBA-15 materials was examined in a semi-batch reactor. The amount of Pd/SBA-15 catalyst was varied from 0.5–1% by weight (wt%) of the SO feedstock. The selectivity of saturated FAMES (C18:0), which contribute to an excellent oxidative stability but undesirable cold flow properties, over the Pd/SBA-15 catalyst at different wt% was poor after a 4-h reaction period. To improve the catalytic performance, zirconium (Zr) species were incorporated in the SBA-15, resulting in Zr-SBA-15 with tunable acidity and pore properties. Partial hydrogenation of SO-FAME over 0.75 wt% Pd/xZr-SBA-15 catalysts (where x is the Zr/silicon (Si) molar ratio and ranged from 0.01 to 0.11) was performed for 2 h. The catalytic performance and the selectivity towards *trans*-monounsaturated FAMES (*trans*-C18:1), in terms of the turnover frequency (TOF) and *trans*-C18:1/*cis*-C18:1 ratio, respectively, were considered at 10% and 80% conversion levels of diunsaturated FAMES (C18:2). The incorporation of Zr into SBA-15 resulted in an enhanced TOF due to the greater adsorption of both H<sub>2</sub> and the basic double bonds of FAME molecules on the electron-deficient catalyst surfaces. The TOF for the Pd/xZr-SBA-15 catalysts increased as the Zr/Si molar ratio increased up to 0.07, and then slightly dropped at higher Zr/Si molar ratios, presumably due to the hindrance of adsorbed-reacted FAME molecules with strong adsorption and the worsening of physical properties, i.e. pore width (D<sub>p</sub>). The selectivity towards *trans*-C18:1 was directly correlated with the Zr/Si molar ratio. Since the strong adsorption of FAME molecules took place on the catalyst surface, the high level of *trans*-C18:1 was consequently generated. The oxidative stability of the partially hydrogenated biodiesels was improved by more than four-fold compared to that of the starting SO-FAMES.

## 1. Introduction

The rapidly increasing global population and economic growth over the past few decades have resulted in a corresponding increased demand for electricity, transport and agricultural products based on fossil-fuels. The increased emission of greenhouse gases, mainly as carbon dioxide, derived from fossil-based industries has caused severe problems in environmental pollution and global warming. Within

Thailand, the Royal Thai government recently proposed an Alternative Energy Development Plan (AEDP2015–2036) to focus on the development of a low-carbon society by promoting the use of renewable energy and resources, such as solar, wind, hydro, bio-energy and bio-fuels [1]. Among these, bio-fuels and especially biodiesel are potential candidates for widespread use as an alternative transport fuel owing to its biodegradable nature, sustainable renewability and high cetane number. Specifically, biodiesel has lower exhaust emissions (unburned

\* Corresponding author at: The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Rd., Pathumwan, Bangkok 10330, Thailand.

E-mail address: [apanee.l@chula.ac.th](mailto:apanee.l@chula.ac.th) (A. Luengnaruemitchai).

<https://doi.org/10.1016/j.fuproc.2018.07.014>

Received 29 May 2018; Received in revised form 6 July 2018; Accepted 15 July 2018

0378-3820/ © 2018 Elsevier B.V. All rights reserved.

hydrocarbons and particulate matters) than petroleum-based fuels, which is in accordance with the more earnest environmental emission regulations [2,3].

The commercial production of biodiesel is usually as fatty acid methyl esters (FAMES), formed via the transesterification of vegetable oils with an excess amount of methanol and catalyzed by homogeneous alkali bases under a mild reaction condition (60–80 °C at atmospheric pressure) [4,5]. However, the resulting biodiesel usually has a poor oxidative stability and cold flow properties, limiting its application to being blended with petro-diesel. In general, fuel properties are associated with the structural features of the starting oil or fat, such as the chain length, degree of chain branching and the nature of individual FAME with various numbers of carbon double bonds (C=C). Those biodiesels with a high content of polyunsaturated FAMES have a low oxidative stability, whereas those containing a high content of saturated FAMES have poor cold flow properties. To obtain a high-quality biodiesel with a balanced oxidation stability and cold flow property, upgraded biodiesel enriched in monounsaturated FAMES is expected to be suitable for most practical applications, especially high blend fuels [5–7].

Partial hydrogenation of FAMES in the presence of transition metal catalysts has been studied as a means to decrease the level of C=C bonds within the fatty acid chains to form a limited level of saturated FAMES [8,9]. In addition to the degree of hydrogenation, the isomerization of *cis*-monounsaturated FAME to its thermodynamically stable *trans*-configuration during the hydrogenation has to be averted due to its higher crystallization point, which results in worse cold flow properties [9,10].

Recent studies have demonstrated that the supported palladium (Pd) catalysts are able to perform hydrogenation in the oil phase due to their high hydrogen adsorption capacity, and to provide a higher catalytic performance than other active metal catalysts, such as platinum, rhodium, rutherfordium and nickel [9,11–13]. Another considerable and widely studied strategy for improving the catalyst performance in the hydrogenation process is to develop outstanding catalyst supports. The preparation of a mesoporous supporting material with different acidity and pore structures has been investigated recently to further tune the size and surface electronic property of the supported metal catalyst. Mesoporous silica materials, especially SBA-15, are extremely attractive because of their excellent characteristics of a high surface area, high surface-to-volume ratio, highly-ordered porous framework, tunable and uniform mesoporous size, super hydrothermal stability and high capacity to functionalize its surface [14–16]. For example, SBA-15 with its high surface area and narrow pore size distribution contributed greatly to a high Pd dispersion [17], while the well dispersed metal nanoparticles (NPs) on the SBA-15 support promoted a higher affinity towards hydrogen (H<sub>2</sub>) molecules [16].

Nevertheless, the lack of an acidic environment on the pure siliceous SBA-15 limits its utilization in a variety of chemical applications. To overcome this problem, the incorporation of zirconium (Zr) into the SBA-15 framework (Zr-SBA-15) to create potential Lewis acid properties has been extensively applied in many acid-catalyzed reactions, such as oxidation, hydroxylation, transesterification and Fischer–Tropsch synthesis [18–21]. However, the Zr-SBA-15 material has not been broadly applied in the partial hydrogenation of biodiesel. Chen et al. [8] researched the performance of Pd catalysts with various mesoporous supports, SBA-15, Zr-SBA-15 (Zr/Si molar ratio = 0.05) and commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, for upgrading the oxidation stability and cold flow properties of palm oil-derived biodiesel using a continuous fixed-bed reactor. The hydrogenation activity of Pd/SBA-15 and Pd/Zr-SBA-15 were quite high and analogous due to the ultra-small Pd NPs with electron-deficient surfaces. With the higher acidic environment of Pd/Zr-SBA-15, the level of *trans*-monounsaturated FAME produced was slightly greater than that with Pd/SBA-15. Accordingly, the outstanding features of a Zr-SBA-15 support together with its optimum level of acid properties makes it an interesting candidate for enhancing the

performance of Pd catalysts in the partial hydrogenation of soybean oil (SO)-derived FAMES (SO-FAMES).

In this study, the motivation was to improve the characteristics and acid properties of Zr-SBA-15 by Zr incorporation into the silica framework of SBA-15. The Zr-SBA-15 materials were prepared by direct hydrothermal synthesis using a Zr/Si molar ratio range from 0.01–0.11. The reactions were performed in a semi-batch reactor at 100 °C and a 4 bar H<sub>2</sub> atmosphere. The hydrogenation activity was examined in terms of the turnover frequency (TOF), while the selectivity was observed in terms of the ratio of *trans*- to *cis*-monounsaturated FAMES (*trans*-C18:1/*cis*-C18:1 ratio) at low and high conversion levels of diunsaturated FAMES (C18:2). X-ray diffractometry (XRD), nitrogen (N<sub>2</sub>) adsorption-desorption, carbon monoxide (CO) pulse chemisorption, transmission electron microscopy (TEM), temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) and X-ray photoelectron spectroscopy (XPS) analyses were employed to characterize the crystallinity phases, textural and structural properties, metal dispersion and size, acid properties and chemical states of the catalysts. The chemical functional groups and FAME compositions of the feed SO-FAMES and the partially hydrogenated (PH)-biodiesels were analyzed using attenuated total reflectance-Fourier transform spectroscopy (ATR-FTIR) and gas chromatography with flame ionization detection (GC-FID), respectively. In particular, the fuel properties, including the oxidative stability and cold flow properties, were determined according to the standard test methods [22, 23].

## 2. Experimental

### 2.1. Materials and chemicals

A nonionic triblock copolymer Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, M<sub>w</sub> = 5800), which was utilized as an organic structure directing agent, was obtained from Aldrich. Tetraethyl orthosilicate (TEOS, 98%) and ZrOCl<sub>2</sub>·8H<sub>2</sub>O, which were used as the silica source and the zirconium precursor, were purchased from Fluka and Acros, respectively. Hydrochloric acid (HCl) was bought from Quality Reagent Chemical (QRc). Palladium ammonium chloride (Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>·xH<sub>2</sub>O), used as the Pd precursor, was acquired from N.E. Chemcat Corporation, Japan. The SO used as the starting material for transesterification, was bought from the Thai Vegetable Oil Co. Ltd. Methanol (analytical reagent grade) and potassium hydroxide (KOH; 85%) were purchased from RCI Labscan Limited, whilst *n*-heptane (analytical reagent grade) was obtained from Fisher Scientific. Other chemical reagents, including sodium sulphate anhydrous (Na<sub>2</sub>SO<sub>4</sub>; 99%) and sodium chloride (NaCl) were bought from Ajax Finechem Pty. Ltd.

### 2.2. Synthesis of the mesoporous support

#### 2.2.1. SBA-15

The parent SBA-15 sample was synthesized by a hydrothermal process as previously reported [24]. In a typical synthesis procedure, a solution of P123 (1 g), deionized water (40.6 g) and 2 M HCl solution (40 g) were prepared in a sealed bottle at 35 °C. After that, TEOS (2.1 g) was added dropwise into the prepared solution and maintained at 35 °C for 24 h to give a milky solution mixture with a molar ratio of 0.017 P123: 1.0 TEOS: 7.9 HCl: 221 H<sub>2</sub>O. This was then transferred into a 125-mL Teflon-lined stainless-steel autoclave and aged at 100 °C for another 24 h. The dispersed particles were harvested by filtration, washed with a large amount of deionized water, dried at 100 °C overnight and then calcined in air at 500 °C for 12 h at a 1 °C/min heating rate.

#### 2.2.2. xZr-SBA-15

The Zr was incorporated into the synthesized SBA-15 by direct hydrothermal treatment as previously reported [25] and described in detail [26], using various molar ratios of Zr/Si (0.01 to 0.11). The Zr-

Download English Version:

<https://daneshyari.com/en/article/11000612>

Download Persian Version:

<https://daneshyari.com/article/11000612>

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