Applied Catalysis A: General 520 (2016) 170–177

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Influence of Mg modifier on *cis-trans* selectivity in partial hydrogenation of biodiesel using different metal types

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ARTICLE INFO

Article history:
Received 19 January 2016
Received in revised form 18 April 2016
Accepted 19 April 2016
Available online 22 April 2016

Keywords:
Biodiesel
Partial hydrogenation
Selectivity
Oxidative stability
Cold flow properties
Mg

ABSTRACT

The catalytic performance of Pd, Pt, and Ni supported on SiO_2 catalysts was investigated for partial hydrogenation of soybean methyl esters, in terms of FAME composition and biodiesel properties, especially oxidative stability and cold flow properties. The effect of Mg modifier over SiO_2-supported catalysts on *cis-trans* selectivity of polyunsaturated FAMEs was also examined. The catalytic testing was performed under reaction conditions of 4 bar hydrogen pressure and 80–120 °C. Hydrogenation activity was presented by turnover frequency (TOF) of diunsaturated fatty acid (C18:2) within 4 h of the reaction time. The highest TOF was obtained over Pd catalysts, while the lowest TOF was obtained from Ni catalysts. At high reaction temperature conditions showed a large amount of *cis*-monounsaturated fatty acid (*cis*-C18:1); however, it exhibited a large amount of *trans*-monounsaturated fatty acid (*trans*-C18:1) which has a negative impact on biodiesel properties. The XPS revealed that the introduction of Mg leads to a strong metal–support interaction caused by electron transfer from the support to the metal, which decreased *trans*-C18:1 formation and presented the higher oxidative stability than the catalysts without Mg modifier.

1. Introduction

The energy demand of the world has dramatically increased due to an increase in population, industrial development, agricultural sector, and transportation. The petroleum fuel has been depleted day by day. Therefore, identifying an alternative source is extremely important. Biodiesel seems appropriate because it is made from renewable biological sources. Besides, it has lower emission profiles, namely un-burned hydrocarbons and particulate matters as compared to petroleum fuel. Therefore, it is an alternative fuel which is in accordance with the strict environmental emission regulations nowadays [1–3].

Biodiesel or fatty acid methyl ester (FAME) can be produced by transesterification of animal fats or vegetable oils with alcohol in the presence of a catalyst. In general, the alcohol used for transesterification is methanol or ethanol, where methanol is the most common because of its low reaction temperature, fast reaction time, high quality products, and low cost [4,5]. Biodiesel has a lot of advantages including economic aspect, such as low production cost, thus it has been increasingly produced worldwide [6]. However, there are some main drawbacks related to its properties especially oxidative stability and cold flow properties. These properties strongly depend on the fatty acid composition of the feedstock since it is identical to that of the resulting biodiesel [7]. The presence of polyunsaturated FAMEs causes low oxidative stability, which makes it difficult to store and consequently influences the overall quality [8,9]. On the contrary, the high amount of saturated FAMEs exhibits the negative effect on cold flow properties, leading to fuel blockage in the fuel systems of the vehicles [10]. Many researchers suggested that monounsaturated FAMEs are the ideal compositions of biodiesel in terms of the above fuel properties [11–14]. Partial hydrogenation is practically employed to transform polyunsaturated FAMEs into monounsaturated FAMEs. Nevertheless, another drawback of partially hydrogenated biodiesel is transformation from *cis*-isomer to *trans*-isomer during reaction proceeding. In addition, due to increasing concern about the negative effect of

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http://dx.doi.org/10.1016/j.apcata.2016.04.019
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trans fatty acids on health, it led to an interest in reducing *trans* fatty acids in hydrogenated vegetable oil. As compared to that of *cis*-isomer, it is less desirable composition because of its higher crystallization point, which also concerns with cold flow properties [15]. Therefore, partial and selective hydrogenation of polyunsaturated FAMEs to *cis*-monounsaturated FAMEs is introduced to improve biodiesel quality.

Many researchers stated that reaction condition was the one important factor affecting on reaction rates and *cis-trans* isomerization. The reaction which proceeded at higher temperature showed the high activity toward both hydrogenation and *trans*-isomerization [16–18]. Moreover, McArdle et al. proposed that the way to reduce *trans*-isomer can be obtained by using high hydrogen pressure (around 10 bar) and low reaction temperature (around 100 °C) [19]. Many literature data reported the use of alkali metals as promoters in many purposes; for example, Fischer–Tropsch synthesis [20], methanol synthesis [21], ammonia synthesis [22], and water–gas shift reaction [23]. However, there are only a few researches related to *trans*-isomer reduction by using promoters. It was reported that a modification in the electronic density of the metallic phase and/or a modification in the acid-base properties led to the adsorption-desorption equilibria of the adsorbed species [24,25]. In the past few years, Tonetto et al. studied the *trans*-isomer reduction in partial hydrogenation of sunflower oils using a Pd/γ-alumina catalyst modified with two promoter types, ethyl benzoate and magnesium glycinate. Ethyl benzoate promoted *trans*-isomer formation, while the magnesium glycinate could reduce it [26].

The catalysts used in partial hydrogenation are normally nickel (Ni) catalysts supported on silica (SiO_2). Ni based catalysts are the most commonly used for vegetable oil hydrogenation due to their low cost compared to noble metal catalysts; however, they require relatively severe operating conditions [27]. In addition, they also facilitate the isomerization of naturally occurring *cis*-isomer to *trans*-configuration during hydrogenation [28]. Hence, noble metals, commonly palladium (Pd) and platinum (Pt), are widely used instead of Ni due to their high activities, and mild hydrogenation process [29–31]. It has been accepted that Pt based catalysts produce lower quantity of *trans* fatty acids [19,32]. Among the various supports, SiO_2 seems to be in demand for any reactions including partial hydrogenation [11,32–35]. It has high surface area, uniform mesoporous channels, and large pore volume, which facilitates the adsorption and dispersion of metal, and also has higher relative stability faced to reduction [36,37].

Soybean oil is one of the promising feedstock for biodiesel production; however, its high contents of polyunsaturated FAMEs are the undesired compositions. The objective of this study was to improve the properties of biodiesel derived from soybean oil by partial hydrogenation, especially oxidative stability. The effect of reaction temperature, 80–100 °C, over three metal types: Pd, Pt, and Ni supported on SiO_2 on hydrogenation activity and *cis-trans* selectivity was determined. In addition, the effect of magnesium promotion on the *trans*-isomer reduction of the prepared catalysts was also investigated. Several techniques have been applied to understand the effects of doping agents of metallic catalysts, including XRD, XPS, AAS, N_2 adsorption-desorption, CO pulse adsorption technique, and CO_2-TPD. The biodiesel properties, oxidative stability and cold flow properties, were also examined.

2. Materials and methods

2.1. Materials

Soybean oil, obtained from Thai Vegetable Oil Public Company Limited, was used as starting material for biodiesel production since it contains high amount of polyunsaturated FAMEs, especially linoleic (C18:2) which causes low oxidative stability. The $Ni(NO_3)_2{\cdot}6H_2O$, purchased from Wako Pure Chemicals Industries Limited, was used as Ni precursor. $Pd(NH_3)_4Cl_2{\cdot}xH_2O$ and $Pt(NH_3)_4Cl_2{\cdot}xH_2O$, obtained from N.E. Chemcat Corparation, Japan, were applied as Pd and Pt precursors, respectively. A commercial mesoporous silica (Q30), which was purchased from Fuji Silysia Chemical Company Limited, was used as a solid support for this study. In addition, magnesium nitrate hexahydrate (Mg modifier), obtained from Sigma-Aldrich Pte Limited, was utilized for study the *trans*-isomer reduction.

2.2. Catalyst preparation

Pd/SiO_2, Pt/SiO_2, and Ni/SiO_2 catalysts were prepared by incipient wetness impregnation method using $Pd(NH_3)_4Cl_2{\cdot}xH_2O$, $Pt(NH_3)_4Cl_2{\cdot}xH_2O$, and $Ni(NO_3)_2{\cdot}6H_2O$, respectively. The metal loading for Pd was 1% (w/w), which was equi-molar to 1.82% (w/w) for Pt. For Ni catalyst, the metal loading was increased to 10% (w/w) due to its low activity. First, SiO_2 support was dried in an oven overnight to remove adsorbed water. Then, it was impregnated with a solution containing metal precursor for 24 h. Next, the catalyst was dried by a rotary evaporator with 3 steps; at room temperature for 2 h, at 60 °C for 2 h, and vacuum pump at 60 °C for 2 h. After that, it was calcined at 300 °C (Pd and Pt) and 450 °C (Ni) for 3 h. The catalyst was reduced at 300 °C (Pd and Pt) and 400 °C (Ni) for 2 h prior to testing in partial hydrogenation.

$Pd\text{-}Mg/SiO_2$, $Pt\text{-}Mg/SiO_2$, and $Ni\text{-}Mg/SiO_2$ catalysts were also prepared by incipient wetness impregnation. The metal loading was 1% (w/w), 1.82% (w/w), and 10% (w/w) for Pd, Pt, and Ni, respectively. The Mg loading was 4% (w/w) using $Mg(NO_3)_2{\cdot}6H_2O$ precursor. First, SiO_2 support was impregnated with a solution of metal precursor (Pd, Pt, Ni) and then it was dried and calcined as previously described. Afterwards, it was impregnated again with a solution of Mg for 24 h and dried by rotary evaporator. Finally, it was calcined at 500 °C for 4 h and reduced prior to testing in the reaction (Supplementary data).

2.3. Catalyst characterizations

The crystallinity and composition in the crystalline phases were identified by X-ray diffraction (XRD), a Rigaku DMAX 2200HV. An X-ray source, generated from a ceramic X-ray tube, was 1.5405 Å CuKα radiation. The instrument was carried out at 40 kV and 30 mA, scan speed of 5/sec, and 2θ of 10–80 .

The chemical states of catalytic materials before and after reaction analyzed by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). The procedure was performed with a monochromatic Al Kα radiation at 15 kV under pressure lower than 5×10^{-7} torr. The binding energy of C1s band at 284.6 eV was applied as a reference.

The actual amount of metal loading was determined by Atomic absorption spectroscopy (AAS), Varian Model SpectraAA30 equipped with a GTA 110 graphite furnace. A deuterium lamp was used as background correction system. The metal concentration was calculated from an analysis curve after calibration with known concentration samples.

The specific surface area, average pore size, and total pore volume of catalyst were investigated by N_2 adsorption-desorption using Surface area analyzer (SAA), Quantachrome Autosorb–1 MP. The catalyst sample was outgassed under vacuum at 250 °C overnight in order to remove the volatile species, prior to measurement.

Metal dispersion was measured by CO pulse adsorption technique using Temperature-programmed desorption/reduction/oxidation (TPD/R/O), Ohkura R6015. Pd and Pt