The Stability of the Palladium-Magnesium Supported on Silica Catalyst for Partial Hydrogenation of Biodiesel

Jakkrapong Jitjamnong [a,*], _Apanee Luengnaruemitchai_ [b]

[a] Petroleum Technology Program, Faculty of Industrial Education and Technology, Rajamangala University of Technology Srivijaya
[b] The Petroleum and Petrochemical College, Chulalongkorn University

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ABSTRACT

Fatty acid methyl ester (FAMEs) has emerged as one of the most potential renewable energy for petroleum derived diesel. The main drawbacks of biodiesel consisted of lower oxidative stability and poorer cold flow properties. Therefore, partial hydrogenation of polyunsaturated FAMEs to _cis_-monounsaturated compound can substantially increase fuel quality. This research was studied on stability of the bimetallic catalysts for partial hydrogenation of FAMEs. Biodiesel derived from soybean oil was used as a feedstock. The partial hydrogenation was carried out on palladium-magnesium catalyst supported on silica. The catalyst was prepared by incipient wetness impregnation method. The metal loading was 1 wt.% for palladium and 4 wt.% for magnesium and they were characterized by using GC, XRD, and BET. The reaction of the partial hydrogenated biodiesel was performed at 4 bar hydrogen pressure, 80 °C temperature. The results indicated that at 10 h of reaction time exhibited the highest the amount of _cis_-monounsaturated. Since, it could convert both triunsaturated and diunsaturated after that it slightly decreased. It means that, the amount of _trans_-monounsaturated content also increased together with the increased of _cis_-monounsaturated content.

*Alekjakkrapong@gmail.com

INTRODUCTION

Currently, environmental pollution with emissions of unburned hydrocarbon, carbon monoxide, nitrogen oxides, and particulate matters as compared to fossil fuel and depletion in reserve of petroleum fuel sources has been a hot issue. Therefore, an alternative fuel is extremely important the use of biofuels in order to replace the fossil fuel. Biodiesel have been accepted as a potential source for sustainable biofuels production since it reduces major environmental concerns. Biodiesel or fatty acid methyl ester (FAMEs) produced by the process of via transesterification in the presence suitable of an alkali catalyst like a potassium hydroxide by using various sources, including edible and non-edible vegetables, waste cooking oils, and animal fat as a feedstock. In addition, biodiesel is completely strong properties over petroleum diesel due to its non-toxicity, renewability, biodegradability, environmental friendly, higher cetane number, and reduced greenhouse gas emissions. Nevertheless, biodiesel are some with several drawbacks and desirable quality, like more susceptible to oxidative and poorer cold flow properties. Degree of saturated fatty acid methyl ester has strongly effects on oxidative stability and cold flow properties, so these properties significantly strong depend on the composition of fatty acid methyl ester. Biodiesel with the high amount of unsaturated fatty acid enhance cold flow

properties but worsen the oxidative stability. On the other hand, the high level of saturated fatty acid methyl ester causes poorer cold flow properties. Many researchers suggested that biodiesel with a high amount of monounsaturated fatty acid methyl ester is valuable component especially the *cis*-C18:1 since it can be enhance the resistance to oxidative degradation and also significantly improve cold flow properties (Devi *et al*., 2017; Sierra-Cantor *et al*., 2017). Partial hydrogenation reaction of polyunsaturated FAMEs to monounsaturated FAMEs compounds can be the solution to enhance the high quality biodiesel, which decrease the degree of polyunsaturated fatty acid methyl ester without increasing the fully saturated FAMEs. In general, partial hydrogenation reaction catalyzed by the noble metal such as palladium (Pd) and platinum (Pt) have good activity and selectivity. Furthermore, bimetallic based catalyst especially Pd-Mg supported on silica catalyst have recently been tested on *cis-trans* selectivity in partial hydrogenated of FAMEs, it showed the highest of *trans*-monounsaturated FAMEs reduction. Furthermore, it enhanced the selectivity toward *cis*-monounsaturated FAMEs (Thunyaratchatanon *et al*., 2016; Numwong *et al*., 2012). Therefore, the present work studies the stability of the bimetallic catalyst supported on silica on *cis-trans* selectivity for partial hydrogenation of FAMEs derived from soybean oil as a feedstock. The stability test was carried out over 24 h. Palladium-magnesium (Pd-Mg) catalyst was prepared by incipient wetness impregnation (IWI). The metal loading was 1 wt.% for palladium and 4 wt.% for magnesium catalyst. The catalyst and product was characterized by using GC, BET, and XRD, respectively.

EXPERIMENTAL

A. Materials
Soybean oil was used as feedstock for biodiesel production, which was obtained from Thai Vegetable Oil Co., Ltd. A commercial silica (SiO$_2$-Q30) with an average pore diameter of 30 nm was used as a solid support, which was purchased from Fuji Silysia Chemical Company Ltd. Pd(NH$_3$)$_4$.Cl$_2$.xH$_2$O (Pd:40.16%) was used as a Pd precursor, which was purchased from N.E. Chemcat Corparation, Japan. On the other hand, Mg(NO$_3$)$_2$.6H$_2$O (99%) purchased from Sigma-Aldrich Pte Ltd. was used as a Mg precursor.

B. Transesterification of Soybean Oil

The biodiesel was produced through the transesterification of soybean oil as raw material, which was used potassium hydroxide (KOH) as a catalyst. 50 g Soybean oil was took place into three-necked round bottom flask, equipped with a stirrer and a condenser and heated to 60 °C. The mixture of methanol and KOH catalyst was prepared by using 16.9 g methanol (the reaction utilized a molar ratio of methanol to oil 9:1) and 0.5 g KOH (the amount of catalyst was used 1 wt.% of soybean oil). The mixture solution was stirred at 300 rpm, 60 °C for 1 h and cooled down. The solution was separated into 2 phases after leave it for 1 night. A phase separation was followed; the lower glycerine phase was removed, and the top ester phase was washed with 60 °C distilled water several times to remove contaminates. The FAMEs composition of biodiesel was characterized by gas chromatography (GC).

C. Catalyst Preparation

The metal loading for Pd was 1 wt.% (w/w) on the silica catalyst was prepared by incipient wetness impregnation method using $Pd(NH_3)_4.Cl_2.xH_2O$ as a precursor. Firstly, silica support was dried at 110 °C for overnight in an oven to remove the absorbed water. Next, the support was impregnated with a solution of Pd precursor for 24 h at room temperature. After that, the catalyst was dried for 6 h. Then, it was calcined at 300 °C for 3 h afterwards the catalyst was impregnated with an aqueous solution of Mg precursor. The Mg loading was 4 wt.%. After impregnation, the $Pd-Mg/SiO_2$ was dried by a rotary evaporator at room temperature for 2 h, at 60 °C for 2 h, and by a vacuum pump at 60 °C for 2 h, respectively. Subsequently, the catalyst was calcined at 500 °C for 3 h under an oxygen flow. Ultimately, the catalyst was reduced at 100 °C for 30 min with a heating rate of 5 °C/min and 100 ml/min hydrogen flow rate prior to catalytic testing in partial hydrogenation reaction.

D. Catalyst Characterization

Rigaku X-ray diffractometer was used characterize the internal structure and crystallinity of the catalyst. Cu Kα radiation (1.5405 Å) was used as an X-ray source to obtain the XRD pattern at running condition for the X-Ray tube of 40 kV and 30 mA. The detector scanned the intensity of diffracted radiation from the $Pd-Mg/SiO_2$ catalyst as a function of 2-Theta in the range of 10° to 80° with a scan speed of 5°/s. A Quantachrome Autosorb-1 MP surface area analyzer was used identify the specific surface area, pore volume, and pore size distribution of support and catalyst. Before testing, the volatile species adsorbed on the catalyst surface was heated under vacuum atmosphere at 250 °C for 24 h.

E. Partial Hydrogenation of Biodiesel

Partial hydrogenation of soybean oil methyl esters was carried out in stainless steel reactor at 80 °C and 4 bars of hydrogen pressure. The amount of catalyst 1 wt.% was added in the semi-batch reactor and the system was purged with nitrogen for air removal. Then, soybean oil biodiesel 150 ml was fed into the reactor. Hydrogen gas was flowed into the reactor with the flow rate of 150 ml/min. Subsequently, the conditions of reaction were increased up to the desired points. Partial hydrogenation step, the stirrer was set at 1,000 rpm to mix the FAMEs, catalyst, and hydrogen gas thoroughly to prevent external cluster transfer. Eventually, the sample was collected every 2 h for 24 h. Gas chromatography (GC) equipped with a FID detector was applied to characterize the biodiesel sample by using n-heptane as a solvent.

RESULTS AND DISCUSSION

A. Catalyst Characterization

The characteristics of the catalyst were obtained using X-ray diffractometer and BET surface area analyzer. The major diffraction peak of the reduced stage of Pd-Mg supported on silica was demonstrated in Fig. 1. The broad peak at 2 theta exhibited of 21.6, suggesting that the mesoporous silica support. The peak was observed at 2 theta of 40.10 and 46.55, corresponding to the palladium metallic. According to Thunyaratchatanon et al., 2016, the characteristic peaks of Pd0 including plane (1 1 1) and (2 0 0) were found at 2 theta of 40.13 and 46.80, respectively. Autosorb-1 MP surface area analyzer was

analyzed the surface area, total pore volume, and pore diameter was summarized in Table 1. For palladium-magnesium catalyst, the surface area, total pore volume, and pore diameter was 107 (m^2/g), 1.17 ml/g, and 43.6 nm, respectively. The catalyst was impregnated on support (SiO$_2$) the surface area insignificantly increased as compared with pure silica. On the contrary, both of total pore volume and pore diameter of palladium-magnesium catalyst slightly decreased as compared with silica support. It evidently displayed that some metal deposition in pores of support.
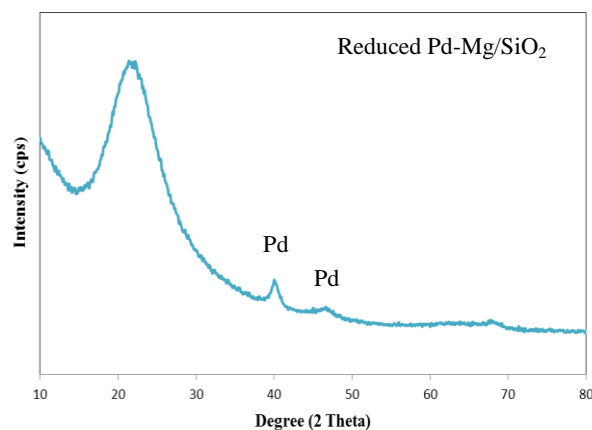

Fig. 1 XRD pattern of Palladium-Magnesium supported on silica.

Table 1 Expected metal loading, surface area, total pore volume, and pore diameter of catalyst and support

Catalyst	Expected metal loading (wt.%)	Surface area (m^2/g)[a]	Total pore volume (ml/g)[a]	Pore diameter (nm)[a]
SiO$_2$		106	1.26	47.5
Pd-Mg/SiO$_2$	Pd = 1.0 Mg = 4.0	107	1.17	43.6

[a] Surface area, total pore volume, and average pore diameter, measured by BET.

B. Partial Hydrogenation of Biodiesel

Fatty acid methyl ester (FAMEs) compositions of soybean oil biodiesel were methyl myristate (C14:0), methyl palmitate (C16:0), methyl palmitelaidate (*trans*-C16:1), methyl palmitoleate (*cis*-C16:1), methyl heptadecanoate (C17:0), methyl stearate (C18:0), *trans*-methyl elaidate (*trans*-C18:1), *cis*-methyl oleate (*cis*-C18:1), methyl linoleate (C18:2), methyl linolenate (C18:3), methyl arachidate (C20:0), methyl *trans*-eicosenoate (*trans*-C20:1), methyl *cis*-eicosenoate (*cis*-C20:1), methyl behenate (C22:0), and methyl lignocerate (C24:0), respectively, it was evaluated FAMEs compositions after partial hydrogenation for 24 h, as represented in Table 2. It could be clearly seen that the amount of total fatty acid was 94.18-98.75%. A configuration of *cis-trans* isomers also has an effect on biodiesel quality. After partial hydrogenation, the content of *cis*-monounsaturated (*cis*-C18:1) is preferable component, which had well fuel quality. On the contrary, *trans*-

isomers are the undesired composition causing significantly increase a melting point of oil (Thunyaratchatanon *et al*., 2016). A 1 wt% Pd-4 wt% Mg loading supported on silica at 10 h of hydrogenation reaction established the best performance in term of *cis*-monounsaturated of the catalyst at 80 °C, 4 bar hydrogen pressure, and 1 wt.% of tested catalyst compared to feed biodiesel. After 10 h of reaction time the content of *cis*-C18:1 rapidly decreased and eventually reached 32.07% within 24 h since the content of unsaturatued of FAMEs completely converted to saturated fatty acid methyl ester, as demonstrated in Fig. 2 (a). It was noteworthy to also mention that, the high amount of saturated FAMEs affects the cold flow properties of fuel. In addition, it was found that the quantity of *trans*-monounsaturated fatty acid methyl ester steadily increased and nearly approach 41.95 % within 24 h, as exhibited in Fig. 2 (b) due to *trans*-isomer was more thermodynamically favored configuration than *cis*-isomer (Thunyaratchatanon *et al*., 2016).

Table 2 FAMEs composition after partial hydrogenation at a condition of 80 °C, 4 bar hydrogen pressure, 150 ml/min hydrogen flow rate, 1000 rpm stirring rate and 1 wt.% of catalyst for 24 h.

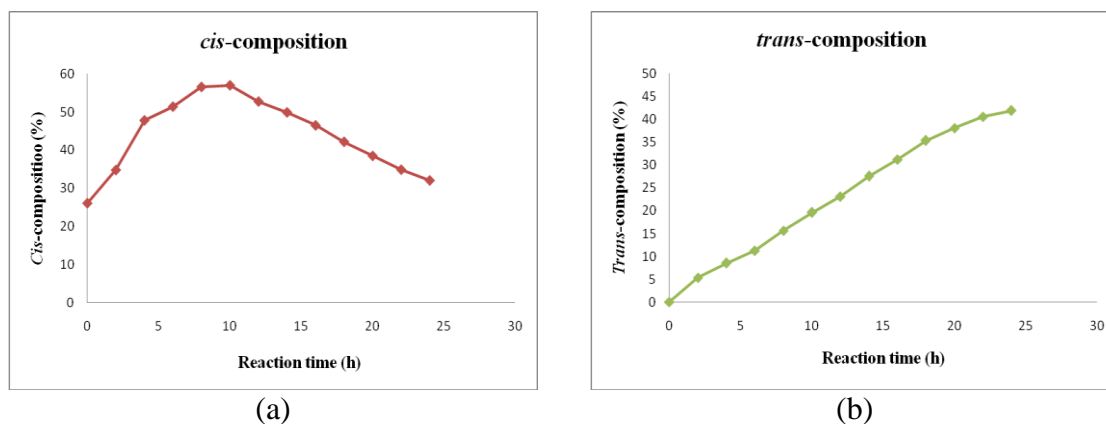| Reaction time (h)	FAMEs (%)
0	98.2479
2	98.5728
4	98.3389
6	97.9933
8	98.3886
10	98.4663
12	94.1754
14	96.7637
16	97.2345
18	98.1399
20	98.0556
22	98.4896
24	98.7487

Fig 2 C18 FAMEs composition of biodiesel after 24 h hydrogenation reaction : (a) *cis*-composition and (b) *trans*-composition

CONCLUSIONS

Partial hydrogenation of soybean oil as a feedstock biodiesel over Pd-Mg catalyst supported on silica, the content of FAMEs was 94.18-98.75% within 24 h of reaction time. The amount of *cis*-monounsaturated FAMEs (C18:1) slightly enhanced and eventually reached 57.05% within 10 h afterwards it rapidly decreased and eventually reached 32.07% within 24 h. Meanwhile, it was completely converted saturated FAMEs which, affects the poorer clod flow properties of biodiesel. Importantly, it was found that *trans*-monounsaturated quantity steadily enhanced within 24 h, which causing an increase in melting point of biodiesel. In addition, it was found that the Pd-Mg catalyst at 10 h exhibited the highest stability since it showed the highest *cis*-monounaturated FAMEs content.

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