

# Deoxygenation of Beef Fat over Pd Supported Mesoporous TiO<sub>2</sub> Catalyst Prepared by Single-Step Sol-Gel Process with Surfactant Template

Tossaporn Jindarat, Siriporn Jongpatiwut, Somchai Osuwan, Suchada Butnark

**Abstract**—Deoxygenation of beef fat for the production of hydrogenated biodiesel is investigated in a high pressure continuous flow fixed bed reactor over palladium-supported mesoporous titania catalyst synthesized via a combined single-step sol-gel process with surfactant-assisted templating method (SATM). The catalyst possessed a mesoporous characteristic with high surface area and narrow pore size distribution. The main products of all Pd/TiO<sub>2</sub> catalysts are n-heptadecane (n-C17) and n-pentadecane (n-C15) resulting from decarboxylation/decarbonylation reaction. Pd/TiO<sub>2</sub> catalyst synthesized via a combined single-step sol-gel process with SATM (SSSG) gave higher activity and selectivity to the desired products when compared to IWI/SG-TiO<sub>2</sub> and IWI/P25-TiO<sub>2</sub>, respectively. SSSG catalyst gave the average conversion up to 80-90 % and 80 % for the selectivity in diesel range hydrocarbon. This result may cause by the higher surface area and the ability in dispersion of palladium ion in mesoporous of TiO<sub>2</sub> during sol-gel process.

**Keywords**—Beef fat, Deoxygenation, Hydrogenated biodiesel, Pd/TiO<sub>2</sub>

## I. INTRODUCTION

THE world's economy dramatically grows in the recent century that was driven by two important parts: industry and transportation. Over 90% of the energy used for industry and transportation is derived from petroleum which is the main factor causing serious global problems. Due to the continuous depletion of the world's non-renewable petroleum reserves, increasing of environment concerns and the price volatility of petroleum, there are many efforts to develop the fuels from alternative sources, including renewable resources such as vegetable oils, animal fats or even waste cooking oils. Biodiesel chemically referred to as a fatty acid methyl ester (FAME) is a fuel derived from fats and oils via transesterification process by using methanol (alcohol) at ambient pressure in the presence of hydroxide or, more effectively, alkoxide catalyst. It has recently been considered as the best candidate for a diesel fuel substitution.

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The main advantage of using biodiesel is that it is biodegradable and produces less harmful gas emissions such as sulfur dioxide (SO<sub>2</sub>) [6]. It also reduces net carbon dioxide emissions when compared with petrodiesel fuel. Although biodiesel is considered as a potential sustainable alternative fuel, there are several properties that limit its uses. Biodiesel has low heating value and low oxygen stability.

It can also cause the increasing of nitrogen oxide (NO<sub>x</sub>) emission and the corrosion problem in the engine. Moreover, more than 95% of biodiesel production feedstock comes from edible oils that may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel [8]. Therefore, renewable diesel, green biodiesel or hydrogenated biodiesel has been studied and gained attention in recent years.

Hydrogenated biodiesel obtained from the deoxygenation process of vegetable oils or animal fats at elevated temperature and pressure in the presence of a heterogeneous catalyst consists mainly of long-chain alkanes. It can substitute directly for or blend with petrodiesel without modification of vehicle engines or fueling infrastructure. Hydrogenated biodiesel not only reduces the limitations of biodiesel uses, but also possesses many advantages over biodiesel including higher cetane number that provide better vehicle performance, lower cloud point, and lower NO<sub>x</sub> and greenhouse gas emission. It can also be produced domestically from a variety of feedstocks.

In the previous work, Pd supported titanium dioxide (TiO<sub>2</sub>) catalyst was considered as a promising catalyst on the deoxygenation of beef fat for the production of hydrogenated biodiesel because it showed the higher catalytic performance compared with other Pd-supported catalysts.

The main purpose of the present work is to study the effect of catalyst preparation methods over the Pd/TiO<sub>2</sub> catalyst on the deoxygenation of animal fats for the production of hydrogenated biodiesel. Pd supported TiO<sub>2</sub> synthesized via a combined single-step sol-gel process with surfactant assisted templating method (SSSG) was selected for comparative studied with the incipient wetness impregnation (IWI) method on both TiO<sub>2</sub> support prepared by the same sol-gel method and commercial P-25 TiO<sub>2</sub>.

## II. EXPERIMENTAL

### A. Materials

All chemical reagents used for catalyst synthesis were of analytical grade and were used without further purification. Tetraisopropyl orthotitanate [TIPT, Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, Merck],

Laurylamine hydrochloride [LAHC,  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\cdot\text{HCl}$ , Merck], Acetylacetone (ACA,  $\text{CH}_3\text{COCH}_2\text{COCH}_3$ , QrëC), Palladium (II) chloride ( $\text{PdCl}_2$ , Aldrich) and Palladium (II) nitrate hydrate ( $\text{Pd}(\text{NO}_3)_2\cdot x\text{H}_2\text{O}$ , Aldrich) were used. TIPT was used as a titanium precursor for synthesizing the  $\text{TiO}_2$  catalyst. LAHC was used as a surfactant template behaving as both a mesopore-directing agent and a gelation-assisted agent. ACA served as a modifying agent, which was applied to moderate the hydrolysis and condensation processes of titanium precursor. Commercially available  $\text{TiO}_2$  powder, Degussa P-25, was selected for comparative studies of catalytic activity testing with synthesized mesoporous  $\text{TiO}_2$  nanocrystal catalyst.

### B. Catalyst preparation

1 wt% palladium supported titania catalyst ( $\text{Pd}/\text{TiO}_2$ ) was synthesized via a combined single-step sol-gel process with surfactant-assisted templating method in a LAHC/TIPT modified with ACA system denoted as SSSG. Briefly, a specified amount of analytical grade ACA was first introduced into TIPT with the TIPT to ACA molar ratio equal to unity. The mixed solution was gently shaken until homogeneous mixing. Afterwards, a 0.1 M LAHC aqueous solution with pH of 4.2 was added to the ACA-modified TIPT solution, in which the molar ratio of TIPT to LAHC was tailored to a value of 4. The mixture was continuously stirred at 40 °C overnight to obtain transparent yellow sol.

To aged  $\text{TiO}_2$  sol solution, a necessary amount of palladium (II) chloride ( $\text{PdCl}_2$ ) solution for the desired Pd loading of 1 wt% was incorporated, followed by aging at 40 °C for 30 min to acquire a homogeneous solution. Then, the sol-containing solution is placed in an oven at 80 °C for a week in order to obtain complete gel formation. The gel was dried at 80 °C overnight to eliminate the solvent, which is mainly the distilled water used in the preparation of LAHC aqueous solution. The dried gel was finally calcined at 500 °C to remove the LAHC template, and consequently produce the desired Pd-supported  $\text{TiO}_2$  catalysts [14]-[17], [20].

For comparative studies, incipient wetness impregnation (IWI) method was used to load Pd onto  $\text{TiO}_2$  support prepared by the same sol-gel method described above and commercial P-25  $\text{TiO}_2$ , denoted as IWI/SG- $\text{TiO}_2$  and IWI/P25- $\text{TiO}_2$ , respectively. The supports were impregnated with an appropriate amount of palladium (II) nitrate hydrate ( $\text{Pd}(\text{NO}_3)_2$ ) aqueous solution, dried at 80 °C and finally calcined at 500 °C for 4 h.

### C. Catalytic characterization

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior of the catalysts and to obtain their suitable calcination temperature. The dried gel of 5-15 mg was heated from 50 °C to 800 °C with a heating rate of 10 °C/min in a static air atmosphere.

X-ray diffraction (XRD) was used to identify phase and crystallite size of the samples by a RINT-2200 with a Cu tube for generating  $\text{CuK}\alpha$  radiation (1.5406 Å) and a nickel filter,

operated at a generator voltage of 40 kV and a generator current of 30 mA in continuous scanning mode at the rate of 5°/min with scan step of 0.05 (2 $\theta$ ).

A surface area analyzer (Quantachrome/Autosorb 1) was used to obtain the adsorption-desorption isotherms of all the investigated catalysts at a liquid nitrogen temperature of 77 K. The Brunauer-Emmett-Teller (BET) approach using adsorption data over a relative pressure that ranged from 0.05 to 0.35 was employed to determine the specific surface area of all the studied catalyst samples. The Barrett-Joyner-Halenda (BJH) approach was used for calculating the mean pore size and pore size distribution. The samples were degassed at 250 °C for 3 h to remove physisorbed gases prior to the analysis.

### D. Catalytic activity testing

The experiment was carried out in a high pressure fixed bed continuous flow reactor. First, the prepared catalysts were placed in the reactor and reduced by flowing hydrogen at 200 psig, 200 °C for 3.5 h. The deoxygenation was conducted at 325 °C, 500 psig, LHSV of 4 h<sup>-1</sup> and H<sub>2</sub> to feed molar ratio of 30. Then, the stream of 20 vol.% feedstock in n-dodecane was fed to the reactor using a high pressure pump. The flow of carrier gas and the reaction pressure were controlled by a mass flow controller and a back pressure regulator, respectively. The liquid product was collected in a stainless steel cylinder trap at the bottom of reactor.

### E. Feed and product analysis

The beef fat feedstock was analyzed for fatty acids composition following AOAC 996.06 method and was also analyzed by an Agilent Technology 7890A gas chromatograph equipped with flame ionization detector (GC/FID) and cool-on column injector, similar to the liquid products. Typically, the liquid products from deoxygenation reaction had to be dissolved in pyridine and silylated with *N,O*-bis(trimethyl)trifluoroacetamide, BSTFA (Acros Organics, 98+%), in order to improve the chromatographic behavior in GC analysis. The internal standard eicosane, C<sub>20</sub>H<sub>42</sub> (99 % purity, ACROS), was added for quantitative calculations.

## III. RESULTS AND DISCUSSION

### A. Catalytic characterization

The thermal decomposition behavior and the suitable calcination temperature of the catalysts were studied by using thermogravimetry and differential thermal analysis (TG-DTA). Fig.1 shows TG-DTA curve of 1 wt.%  $\text{Pd}/\text{TiO}_2$  catalyst synthesized via a combined sol-gel process with surfactant-assisted templating method. The DTG curve shows two main exothermic regions. The first exothermic peak, with its position between 150 °C and 350 °C, is attributed to the burnout of the surfactant template. The second exothermic peak between 350 °C and 500 °C corresponds to the crystallization process of the support and also the removal of organic remnant and chemisorbed water molecule [5].

The TG result reveals that the weight loss ends at a temperature of approximately 500 °C for SSSG catalyst.

Hence, the calcinations temperature at 500 °C is sufficient for both the complete removal of the organic surfactant molecules and the catalyst crystallization process.

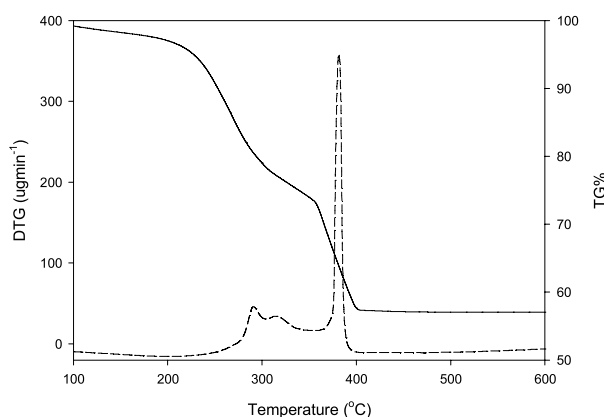


Fig. 1 TG-DTA curve of 1 wt.% Pd/TiO<sub>2</sub> catalyst synthesized via a combined single-step sol-gel process with surfactant-assisted templating method (SSSG)

The adsorption-desorption isotherm of both 1 wt.% Pd/TiO<sub>2</sub> catalyst synthesized via a combined single-step sol-gel process with surfactant-assisted templating method and TiO<sub>2</sub> support prepared by the same method (SG-TiO<sub>2</sub>) reveal the typical IUPAC type IV pattern with the H<sub>2</sub> hysteresis loop, which is associated with capillary condensation taking place in mesopores. Besides, the isotherm also shows the limiting uptake over a range of high relative pressure (P/P<sup>0</sup>) that is another characteristic feature of a mesoporous material, as shown in Fig. 2(a) and 2(b), respectively.

With the commercial P-25 TiO<sub>2</sub> support denoted as P25-TiO<sub>2</sub>, the absence of both a hysteresis loop and an adsorption plateau at very high relative pressure indicates that there is no capillary condensation of N<sub>2</sub> into the pore corresponding to the IUPAC type II that possesses the non-mesoporous characteristic.

The textural properties obtained from the N<sub>2</sub> adsorption-desorption isotherms (i.e., BET surface area, total pore volume, and mean pore diameter) of the catalysts are summarized in Table I.

TABLE I  
TEXTURAL PROPERTIES OF THE CATALYST

Catalyst	Surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Mean pore diameter (nm)
SG-TiO <sub>2</sub>	89.60	0.170	7.61
P25-TiO <sub>2</sub>	50.50	0.230	18.50
IWI/SG-TiO <sub>2</sub>	77.30	0.187	9.66
IWI/P25-TiO <sub>2</sub>	48.80	0.228	18.70
SSSG	113.00	0.203	7.19

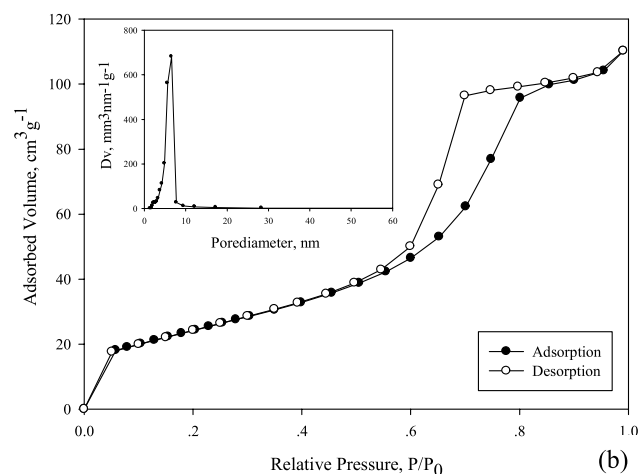
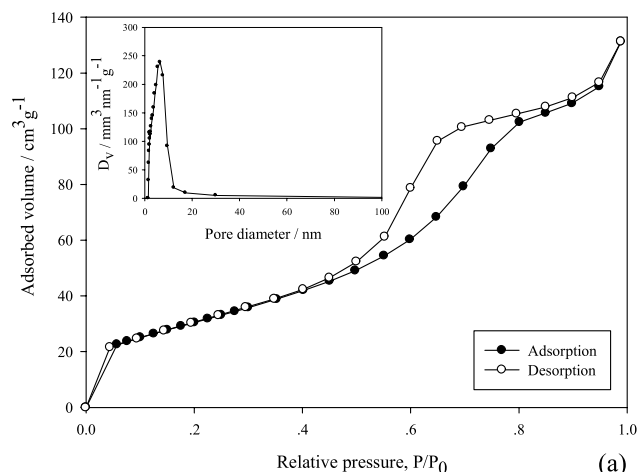


Fig. 2 N<sub>2</sub> adsorption-desorption isotherm of: (a) 1 wt.% Pd/TiO<sub>2</sub> catalyst synthesized via a combined single-step sol-gel process with SATM (SSSG); (b) TiO<sub>2</sub> support prepared by the same sol-gel method (SG-TiO<sub>2</sub>) (inset: pore size distribution)

The XRD patterns of all catalysts were shown in Fig.3. The XRD pattern of the SSSG catalyst, SG-TiO<sub>2</sub> support and IWI/SG-TiO<sub>2</sub> catalyst reveal the crystalline structure of the pure anatase phase owing to dominant peaks at 2θ of 25.2°, 37.9°, 48.3°, 53.8°, 62.7°, 68.9°, and 75.3°, which represent the indices of (101), (103), (200), (105), (213), (116), and (107) planes, respectively. For commercial P-25 TiO<sub>2</sub> and IWI/P25-TiO<sub>2</sub>, the occurrence of the peaks at 2θ of about 27.5°, 36.0°, 41.2°, 44.1°, 54.2°, 56.7°, 64.2°, and 69°, which correspond to the indices of (110), (101), (111), (210), (211), (220), (310), and (301) planes, respectively, indicates that it comprises a mixture of anatase and rutile phases with approximately 78% rutile content that is calculated from XRD intensity data by Spurr and Myers' method.

Nevertheless, the presence of Pd could not be observed at all of the palladium supported titania catalysts, likely due to the combination of their low content, high degree of dispersion and small particle size.

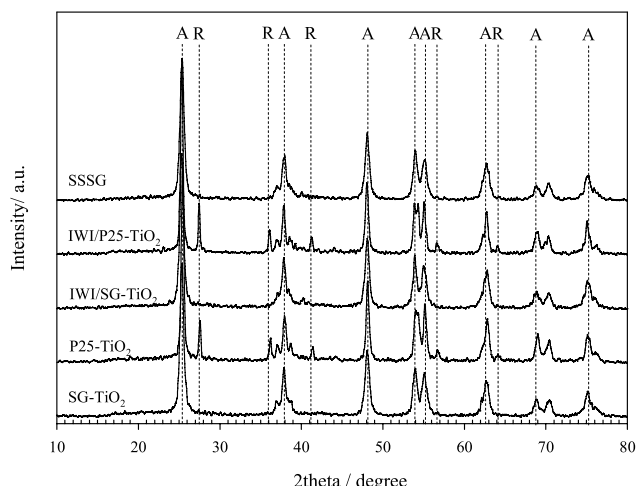


Fig. 3 XRD patterns of SG-TiO<sub>2</sub>, P25-TiO<sub>2</sub>, Pd/TiO<sub>2</sub> catalyst: IWI/SG-TiO<sub>2</sub>; IWI/P25-TiO<sub>2</sub>; and SSSG (A:anatase, R:rutile)

### B. Catalytic Activity

1 wt.% Pd supported TiO<sub>2</sub> catalysts were prepared via a combined single-step sol-gel process with SATM (SSSG) and incipient wetness impregnation (IWI) using both SG-TiO<sub>2</sub> and P25-TiO<sub>2</sub>. The prepared catalysts were tested for their catalytic activity and selectivity in deoxygenation of beef fat towards hydrogenated biodiesel in a continuous flow fixed bed reactor under 500 psig, 325 °C, liquid hourly space velocity (LHSV) of 4 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 30. The results show that the beef fat can be converted to paraffinic hydrocarbons that have carbon atom in diesel specification range (C15-C18 hydrocarbons) over all of the Pd/TiO<sub>2</sub>

catalysts as summarized in Table II. The major products from beef fat are n-heptadecane (n-C17) and n-pentadecane (n-C15), alkane products that have one carbon atom less than the original fatty acids in each oil molecule, indicate that the deoxygenation of beef fat over Pd/TiO<sub>2</sub> catalysts tends to undergo decarboxylation/decarbonylation pathway rather than hydrogenation pathway [7],[14]. 1 wt.% Pd/TiO<sub>2</sub> catalyst synthesized via a combined single-step sol-gel process with SATM (SSSG) was successfully achieved with the higher activity and selectivity to the desired products when compared to IWI/SG-TiO<sub>2</sub> and IWI/P25-TiO<sub>2</sub> catalyst, respectively.

SSSG catalyst gave the average conversion about 80-90 %, 60-70 % and 30-40 % in case of IWI/SG-TiO<sub>2</sub> and IWI/P25-TiO<sub>2</sub> catalysts, respectively. Beside, SSSG catalyst was also an excellent catalyst for selective deoxygenation of beef fat to hydrocarbon in diesel specification range. The selectivity to diesel range hydrocarbon was very high, 80 %, while the selectivity to intermediates (palmitic acid, oleic acid, stearic acid, heavy esters, and diglycerides) was 12-14 %. From the result, it may cause by the highest surface area of SSSG catalyst (113 m<sup>2</sup>g<sup>-1</sup>) among other Pd/TiO<sub>2</sub> catalysts (77.3 and 44.8 m<sup>2</sup>g<sup>-1</sup> for IWI/SG-TiO<sub>2</sub> and IWI/P25-TiO<sub>2</sub>, respectively). Palladium ion tends to well disperse in mesopore of TiO<sub>2</sub> support during sol-gel process with surfactant-assisted templating method.

In case of IWI/SG-TiO<sub>2</sub> and IWI/P25-TiO<sub>2</sub> catalysts, IWI/SG-TiO<sub>2</sub> gave higher conversion and higher selectivity to the desired products as a result of the higher surface area that provide the higher metal dispersion resulting in the larger the fraction of the metal atoms that are exposed at surfaces, where they are accessible to reactant molecules and available for catalysis.

TABLE II  
PRODUCT DISTRIBUTION ON THE DEOXYGENATION OF BEEF FAT OVER Pd/ TiO<sub>2</sub> CATALYST

Catalyst	IWI/P25-TiO <sub>2</sub>			IWI/SG-TiO <sub>2</sub>			SSSG		
	4	5	6	4	5	6	4	5	6
Time on stream (h)	4	5	6	4	5	6	4	5	6
Conversion	33.70	26.09	24.24	71.11	67.75	63.56	84.34	84.01	79.51
Selectivity									
Total C15-C18	50.50	49.70	52.59	66.52	62.92	61.66	82.68	81.82	80.17
n-C15	11.17	11.10	12.53	13.86	12.65	11.56	20.54	20.31	19.82
n-C16	5.31	5.18	4.69	8.77	8.57	8.64	6.88	6.93	7.23
n-C17	24.46	24.17	27.05	28.75	26.67	25.49	43.56	42.78	41.19
n-C18	9.56	9.25	8.32	15.14	15.03	15.97	11.70	11.80	11.93
(C15+C17)/(C16+C18)	2.40	2.44	3.04	1.78	1.67	1.49	3.45	3.37	3.18
Intermediates	45.05	46.11	42.89	28.89	32.67	34.20	12.54	13.18	14.63
Palmitic acid	7.70	7.53	7.22	2.37	2.58	2.56	1.42	1.29	1.36
Oleic acid	2.51	16.82	2.65	0.63	8.41	0.94	0.17	3.64	0.27
Stearic acid	16.59	2.55	16.22	7.13	0.76	9.48	3.37	0.22	3.89
Ester	14.65	14.94	13.90	15.82	18.32	18.40	6.91	7.32	8.19
Diglyceride	3.60	4.27	2.90	2.94	2.60	2.82	0.67	0.71	0.92
Others	4.45	4.19	4.52	4.59	4.41	4.14	4.78	5.00	5.20
n-C13	3.39	3.17	3.55	2.92	2.78	2.57	3.47	3.68	3.79
n-C14	1.06	1.02	0.97	1.67	1.63	1.57	1.31	1.32	1.41

#### IV. CONCLUSIONS

In this work, beef fat can be converted into hydrogenated biodiesel (C15 to C18 hydrocarbons) via deoxygenation reaction in a continuous flow fixed bed reactor under 500 psig, 325 °C, liquid hourly space velocity (LHSV) of 4 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 30. The main products of all Pd/TiO<sub>2</sub> catalysts are n-heptadecane and n-pentadecane resulting from decarboxylation/decarbonylation reaction. 1 wt.% Pd/TiO<sub>2</sub> synthesized via a combined single-step sol-gel process with SATM (SSSG) was successfully achieved with higher activity and selectivity to the desired products when compared to IWI/SG-TiO<sub>2</sub> and IWI/P25-TiO<sub>2</sub> catalysts. The high activity and product selectivity of SSSG could be due to its high surface area and the ability in Pd dispersity.

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