Malaysian Journal of Catalysis 2 (2017) 53-56

Malaysian Journal of Catalysis

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Mesoporous TiO_2: Potential catalyst for deoxygenation of triglyceride to hydrocarbon-like biofuel

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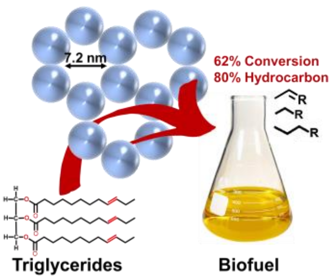
Article history :
Received 6 May 2017
Accepted 27 July 2017

GRAPHICAL ABSTRACT



ABSTRACT

Worldwide environmental concern owing to greenhouse gas emission through combustion of fossil fuel and depletion of fossil fuel urged the need for sustainable biofuel production. Special attention has been given to the deoxygenation, an important method for a sustainable supply of biofuel for future generations. This work reports the deoxygenation of triglycerides to hydrocarbon-like biofuel over commercial nanoparticle TiO_2 (NP-TiO_2) and synthesized mesoporous TiO_2 (M-TiO_2). Mesoporous TiO_2 (M-TiO_2) was synthesized via sol-gel method by addition of triblock copolymer (Pluronic F127) as surfactant. The physicochemical properties of these catalysts were characterized by XRD, BET and Raman spectroscopy. The deoxygenation of triglycerides was studied by using triolein as model compound at 380 °C for 4 h. The major deoxygenated products of the reaction are olefin and paraffin. The synthesized M-TiO_2 catalyst gave higher conversion (62%) as compared with NP-TiO_2 (49%). This result may due to the higher surface area and presence of mesoporosity which improves the diffusional transport of reactants. This study suggests that surface area and porosity play an essential role in determining deoxygenation activities. Mesoporous TiO_2 is a promising catalyst in producing hydrocarbon-like biofuel from triglyceride.

Keywords: *Deoxygenation, Mesoporous TiO_2, triolein, hydrocarbon*

| eISSN 0128-2581 |

1. INTRODUCTION

Biofuels have potential to substitute part of the energy supply and contribute to the reduction of greenhouse gases. Currently, there are only a few methods in producing biofuels. The production of biodiesel from vegetable oils and animal fats by transesterification with methanol represents a well-established means of producing renewable biofuels [1-3]. However, this biodiesel suffers from drawbacks such as poor storage stability and marginal cold flow properties [4]. Consequently, there is growing interest in the development of processes for conversion of fats and oils into hydrocarbon-like fuel. This fuel can serve as a replacement of petroleum-derived fuels. Recent studies have shown that the removal of oxygen from the constituent triglycerides and fatty acids can proceed via a number of parallel pathways, which include decarboxylation (-CO_2), decarbonylation (-CO) and hydrodeoxygenation (-H_2O) reaction [5-7]. This has been an interesting topic for researchers to obtain a feasible renewable biofuel.

Over the past decades, titanium dioxide (TiO_2) has been widely studied as a catalyst support for a variety of clean energy and environmental applications, such as photocatalytic hydrogen production by water splitting, and photodegradation of organic pollutants [8-12]. TiO_2 is regarded as a benchmark due to its high efficiency, non-toxicity, high redox property and good chemical stability [13,14]. Recently, a lot of researches showed that TiO_2 exhibits efficient and selective organic synthesis corresponding to hydrodeoxygenation, transesterification, and hydrogenation [1,15-18]. These findings lead to the new development of TiO_2 in deoxygenation to produce sustainable biofuel.

It is well known that the effectiveness of catalytic processes strongly depends on surface area, pore structure, and chemical composition of the catalyst [19]. High surface area is helpful to obtain more exposed active sites and an enhanced the catalytic activity. As one of the most important influential factors, pore structure, not only affects the specific surface but also influences the diffusion of reactant molecules [20]. Mesopores, in particular, can improve accessibility to acid sites predominantly localized on the surface of TiO_2, thereby overcoming the mass-transport limitation. This feature is paramount important in the reaction involving bulky bio-derived reactants and enhancing catalytic activity [21,22]. Shorter diffusion lengths, and consequent in-pore residence times, may also influence product selectivity through the suppression of secondary reaction pathways [23]. Thus, obtaining synchronous large surface area and high penetrable pore structure catalyst is worth to explore.

In this study, we reported TiO_2 as a catalyst for deoxygenation of triglycerides to produce hydrocarbon-like biofuel. We explore the impact of mesoporosity on the deoxygenation of triolein. The relationship between structure and catalytic activity was correlated via some physico-chemical characterization. We highlighted the influence of mesoporosity on the catalytic activity of TiO_2 catalyst, which has not been investigated yet.

2. EXPERIMENTS

2.1 Materials

Titanium (IV) isopropoxide (TTIP, 97%), anhydrous ethanol (99%), hydrochloric acid (37%) and pluronic F-127 were used in catalyst synthesis. TiO_2 nanoparticles (99.7%) was used as catalyst for the reaction. Glyceryl Trioleate (65%) was used as model compound of triglycerides in deoxygenation. All chemicals were purchased from Sigma-Aldrich and were used as received without further treatment. Mili-Q deionized water was used throughout this study.

2.2 Catalyst preparation

M-TiO_2 was synthesized using a modified sol-gel method. Titanium isopropoxide as the precursor was added to the solution consist of pluronic F-127, ethanol and deionized water, with a molar composition of TTIP : 40 C_2H_5OH : 0.005 F-127 : 15 H_2O. The solution was adjusted to pH 4 and aged for 24 hours at room temperature. The product was recovered by centrifugation, washed repeatedly with distilled water and dried overnight. The dried powder was calcined at 400 °C for 6 hours to remove the triblock copolymer. NP-TiO_2 was prepared from commercial TiO_2 which calcined at 400 °C for 6 hours.

2.3 Catalyst characterization

The crystal structure, crystallite size and crystallinity were analyzed using x-ray diffraction (XRD) Bruker AXS D8 advanced diffractometer with a Cu Kα radiation (α = 1.5406 Å) from 20° to 80° Bragg angle. The BET surface area and mesoporosity were measured using a multi-point nitrogen adsorption–desorption analyzer. Prior the measurement, the samples were degassed at 300 ºC for 4 hours. The pore size distribution was calculated using BJH equation. The Raman spectra were scanned from 100 cm^{-1} to 1000 cm^{-1} using a Renishaw with Ar-ion laser (514 nm) at room temperature.

2.4 Reaction procedure

Deoxygenation reactions was carried out in batch reactor equipped with a temperature controller. The reactor vessel was fitted with a chiller. In a typical reaction, 10 g of reactant (Glyceryl Trioleate) and 5 wt% of catalyst were loaded in the reactor. The temperature of the reactor was raised to 380 °C at a heating rate of 10 °C/min. The reaction was conducted for 4 hours with stirring at 400 rpm. The product was isolated. The conversion of reactant, liquid production rate and liquid yield are calculated based on the equations as follows:

Conversion (%) =

$$\frac{\text{Mole of Reactant}_{\text{i}} - \text{Mole of Reactant}_{\text{f}}}{\text{Mole of Reactant}_{\text{i}}} \times 100\% \qquad (1)$$

$$\text{Liquid Production Rate} = \frac{Mass\ of\ Liquid\ Product}{Time\ of\ reaction} \qquad (2)$$

2.5 Product characterization

The liquid product distribution was analyzed by gas chromatography mass spectrometer (GCMS) technique. A samples were diluted in hexane. A Shimadzu GC 2010-Plus equipped with RTX-5MS capillary column (30.0 m x 0.25 μm x 0.25 mm) was used for the analysis. The oven temperature was raised from 40 °C to 300 °C and hold for 30 min. All MS peaks were compared with NIST standard reference database.

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

Fig. 1 shows the XRD pattern of NP-TiO_2 and M-TiO_2 samples. The results indicated that the NP-TiO_2 sample presented only anatase phase. According to the standard ICDD card No. 00-001-0562, characteristic diffraction peaks for anatase phase of TiO_2 are shown at 2θ = 25.2°, 37.8°, 47.9°, 54.0° and 62.6° which corresponded to (101), (004), (200), (105) and (204) . The diffraction peaks of M-TiO_2 showed mixed phase of anatase and brookite, where 2θ values of 30.8° can be attributed to (121) plane of brookite rutile TiO_2 (ICDD Card No. 00-003-0380) [24]. The weight fractions of the crystal phase were calculated using the Spurr equation, $f_A = 1/(1 + 1.26 \text{ x } I_B/I_A)$, where f_A is the weight fraction of anatase, $f_B = 1 - f_A$ is the weight fraction of brookite, I_A is the intensity of the most intense anatase peak (101), I_B is the intensity of the most intense brookite phase peak (121) and 1.26 is the scattering coefficient [11]. For the M-TiO_2, anatase and brookite fraction are 90% and 10%, respectively. The crystallite size of NP-TiO_2 and M-TiO_2 calculated from major diffraction peak using Scherrer Equation are 29.0 and 12.5 nm, respectively.

The presence of well-ordered mesopores in M-TiO_2 was confirmed by N_2-adsorption studies (Fig. 2). M-TiO_2 (Fig. 2b) showed a type –IV isotherm with a hysteresis loop of H1-type, indicating the existence of ordered mesopores in the materials. The meso-structure in the M-TiO_2 sample gave high specific surfaces area (101.6 m^2/g), high pore volume (0.231 cm^3/g), and uniform pore diameter centered around 7.2 nm (Table 1 and Fig. 3). In contrast, the adsorption isotherm of NP-TiO_2 showed a type-II isotherm indicating non-porous materials (Fig. 2). Obviously, the specific surface area of M-TiO_2 was much higher than the NP-TiO_2 (10.2 m^2/g). By generating mesoporosity in the

TiO_2, the specific surface area has been increased 10 times compared to that of commercial NP-TiO_2.

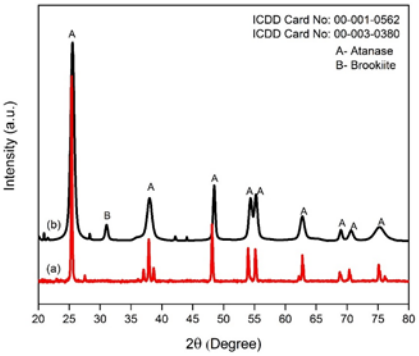


Fig. 1 XRD pattern of (a) NP-TiO_2 and (b) M-TiO_2

Table 1 Textural properties of the catalysts

Sample	S_{BET} (m^2/g)	Pore Size (nm)	Pore Volume (cm^3/g)	d-spacing (nm)	Crystallite Size (nm)ᵃ	Weight fractions of phase (%)ᵃ	
						Anatase	Brookite
NP-TiO_2	10.2	25.9	0.043	0.35	29.0	100	-
M-TiO_2	101.6	7.2	0.231	0.35	12.5	90	10

ᵃ Calculated using Scherrer equation

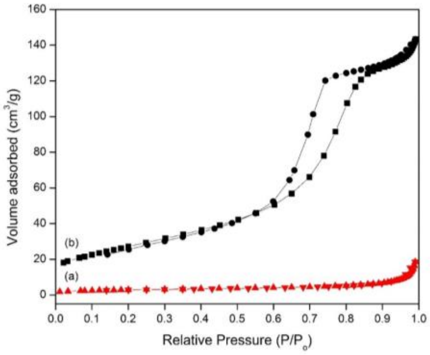


Fig. 2 Nitrogen adsorption-desorption isotherms of (a) NP-TiO_2, and (b) M-TiO_2

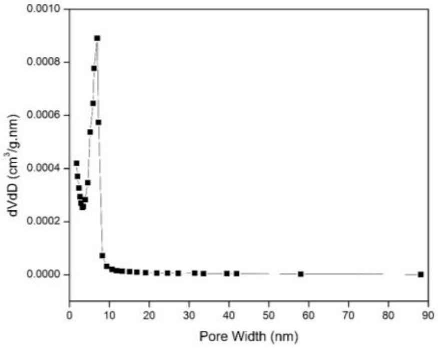


Fig. 3 Pore size distributions of M-TiO_2

Raman spectra of the samples was shown in Fig. 4. NP-TiO_2 (Fig. 4a) exhibit five typical anatase Raman bands at 141 cm^{-1} (E_g), 197 cm^{-1} (E_g), 395 cm^{-1} (B_{1g}), 515 cm^{-1} (A_{1g}), and 637 cm^{-1} (E_g) [25]. Meanwhile, M-TiO_2 (Fig. 4b) exhibited typical feature of anatase and also the presence of brookite phase at 245 cm^{-1} (A_{1g}) and 320 cm^{-1} (B_{1g}). These data are consistent with the XRD results.

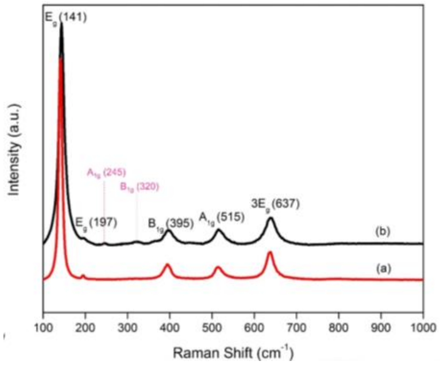


Fig. 4 Raman spectra of (a) NP-TiO_2, and (b) M-TiO_2

Table 2 Comparison of total conversion, production rate and yield of deoxygenation of triolein over TiO_2.

	M-TiO_2	NP-TiO_2
Triolein Conversion (%)	62	49
Liquid Production Rate (mg/min)	19	14
Liquid Product (g)	4.6	3.4

3.2 Deoxygenation Reaction

To investigate the effect of mesoporosity on catalytic activity, deoxygenation of triglycerides at 380 °C for 4 hours was performed over both the NP-TiO_2 and M-TiO_2 catalysts. A reaction without catalyst (blank) was carried out and it was found that the conversion of was only18% at 380 °C after 4 hours. As shown in Table 2, the total conversion of triolein for the M-TiO_2 and NP-TiO_2 catalysts are 62 and 49%, respectively. The liquid production rate and liquid yield of M-TiO_2 (19 mg/min, 2.9 g) is higher compared to that of NP-TiO_2 (14 mg/min, 1.7 g). Clearly, the performance of M-TiO_2 is superior to the NP-TiO_2. According to the foregoing characterization analysis, the main difference between M-TiO_2 and NP-TiO_2 is the existence of mesoporosity and large surface area [20,23]. The selectivity of different fraction present in liquid products are shown in Fig. 5, M-TiO_2 showed highest selectivity to hydrocarbon (80%) and small amount of aldehyde (7%) and acid (13%). The hydrocarbon comprises of unsaturated and saturated hydrocarbon in the range of C8 to C24 (e.g. 8-heptadecene and heptadecane). NP-TiO_2 showed only 67% selectivity to hydrocarbon and relatively high amount of oxygenated compounds (22% of acid, 10% of alcohol and 1% of aldehyde) as intermediates of deoxygenation reaction. In addition, the hydrocarbon in the product is grouped into gasoline range (C8 to C12), diesel range (C13 to C18) and heavy product (C19+). The selectivity of the products was shown in Fig. 6. Both catalyst shows high selectivity towards gasoline range hydrocarbon. Such result suggests that the existence of mesoporosity in TiO_2 able to enhance the diffusional transfer, which improving deoxygenation ability and thus producing high yield of alkanes and alkenes.

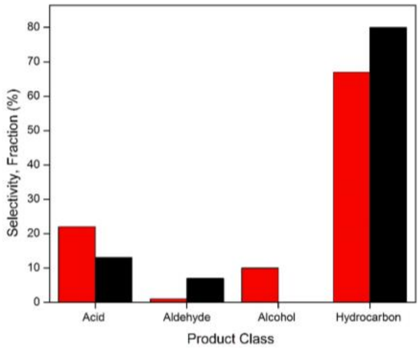


Fig. 5 Classification liquid product (a) NP-TiO_2, and (b) M-TiO_2

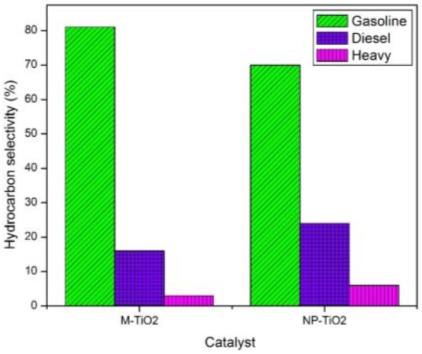


Fig. 6 Selectivity of hydrocarbon from catalytic deoxygenation

4. CONCLUSION

In summary, this paper has investigated the effects of mesoporosity of TiO_2 on their structure and catalytic properties. The mesoporous TiO_2 was successfully synthesized via sol-gel method. It possess large surface area and uniform mesopores (7.2 nm). The results indicate that the existence of mesopores on TiO_2 are contributed to exceptional deoxygenation ability and selectivity towards hydrocarbon. Thus, mesoporous TiO_2 is a promising catalyst to produce hydrocarbon-like biofuel through deoxygenation.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of Malaysia's Fundamental Research Grant Scheme (FP054-2013B and FB056-2013B), SATU Joint Research Scheme (RU020A-2015 and RU018D-2016), University Malaya Research Grant (UMRG RP025A/B/C-14AET), IPPP Postgraduate Research Grant (PG071-2014B) and University of Malaya Fellowship Scheme.

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