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Synthesis and characterization of silica-titania catalyst with solid-state technique applying SiO_2 and TiO_2 solid precursors based on variation time of calcination in biodiesel production

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Abstract. In order to obtain the silica-titania with titanium tetrahedral coordination using solid state method, several parameters which influence the number titanium tetrahedral coordination are still investigated. In the previous study, the effect of mol ratio of Si:Ti and various temperatures for calcination were reported, however, this investigation is related to silica-titania with titanium tetrahedral coordination based on variation time (6 – 8h) of calcination using 1:1 mol ratio of Si:Ti at 450°C. Results show longer calcination time yields higher fraction of titanium tetrahedral with concentration still lower than 41%. The physical properties of biodiesel produced by this own synthesis of silica titania catalyst are influenced by titanium tetrahedral fraction in silica-titania in terms of viscosity, density and acid number and those properties are enhanced by increased fraction of titanium tetrahedral.

1. Introduction

Previous study reported high catalytic activity of TS-1 is influenced by hydrophobic environment and the existence of titanium tetrahedral framework [1]. It has been justified that titanium tetrahedral framework shows better catalytic properties than that of titanium octahedral framework in titano-silica group [2]. The titanium tetrahedral framework is observed as small band absorption related to Si-O-Ti bond in the range of wave number of 980-940 cm^{-1} in infra red region. The FTIR investigation is confirmed by band absorption in wavelength of 200 – 260 nm using DR UV-Vis examination. The fraction number of titanium tetrahedral framework can be determined using deconvolution technique in DR UV-Vis spectra applying Gaussian equation[2].

However, catalytic activity of TS-1 has limitations, therefore, researchers have attempted another investigation applying new silica and titania material referred to titanium tetrahedral framework for several applications [1]. This research group previously investigated the effect of various calcination temperature[3] and mol ratio of Si and Ti on the number of titanium tetrahedral coordination [4] in the synthesis of silica-titania catalyst using solid state and the result showed that mol ratio of Si : Ti (1 : 0.5) yielded the highest number of titanium tetrahedral coordination. In addition, the calcination temperature of

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450^{o}C yielded highest number of titanium tetrahedral. The investigation based on deconvolution spectra shows that the titanium tetrahedral fraction in silica-titania catalyst obtained by variation of mol ratio of Si and Ti, and effect of calcination temperature is generally almost 50%, which is much higher than titanium tetrahedral fraction in its precursor (TiO_2), i.e. 23% [5].

The two series of silica-titania catalyst (effects of mol ratio of Si:Ti and calcination temperature) have already applied for biodiesel production from reaction of palm oil and methanol. The results show a correlation between titanium tetrahedral framework and physical properties of biodiesel (viscosity,density and acid number). In general, viscosity, density and acid number are undergone decreasing from those properties of the original oil due to increasing of titanium tetrahedral fraction. Based on that reason, this study continues to investigate the titanium tetrahedral coordination in the synthesis of silica-titania catalyst using solid state method on the basis of variation of calcination time. The catalyst obtained is applied for biodiesel production.

2. Experimental

2.1. Material
Solid silica and titania were applied in this investigation. Toluene was used as dispersion media. The oil feedstock (palm oil (bimoli), waste cooking oil of palm oil, bulk cooking oil, and waste cooking oil of bulk cooking oil) and methanol were used for biodiesel production.

2.2 Instrumentation
This study used glassware for synthesis, ultrasonic, and devices as FTIR and DR UV-Vis for characterizations.

2.3 Synthesis of Silica-Titania catalyst
The synthesis of silica-titania catalyst followed the previous procedure [3][4]. Respective silica and titania precursors with mol ratio of 1:1 were dissolved in 10 ml toluene. Then the mixture was sonificated for 1h in an ultrasonic bath. After that, the mixture was removed from ultrasonic and placed in a fume-hood and abandoned for 24h to evaporate toluene. The mixture of silica and titania was calcinated at 450oC for 6, 7, and 8h, respectively. The three variations of time were selected on the basis of general calcination used for systhesis of material. Samples obtained from clacinations were stored in a dessicator to prevent adsorption of water vapor and air on sample surface prior to characterizations and application for biodiesel production.

2.4 Characterizations of silica-titania catalyst
The samples of silica-titania obtained were characterized by FTIR and DR UV-Vis. The FTIR characterizations were detected at wave number 1500 – 400 cm^{-1}. The main vibration frequencies were observed for Si-O-Si, Ti-O-Ti, and Si-O-Ti. The DR UV-Vis characterizations were conducted at wavelength range of 200-400 nm. The UV spectra were deconvoluted using Gaussian equation.

2.5 Application of silica-titania catalyst for biodiesel production
The synthetic silica-titania catalysts from solid precursor of silica and titania were applied for biodiesel production from 2 types of oil, i.e. palm oil and bulk cooking oil (Table 1). In general, the biodiesel production obtained from reaction of raw oil and methanol in reflux system. The mol ratio of oil and methanol is to be 1:6. The mol ratio of catalyst and oil is to be 1:10 (10%). The reaction was done at 65^{o}C for 3h stirring with a magnetic stirrer. At the end of reaction, the catalyst was removed by centrifugation and followed by evaporation of methanol residue using rotary evaporator. In order to justify that the raw

oil has already converted to biodiesel, the product was examined based on its physical properties and compared its properties to that of original oil. The physical properties are related to acid number, viscosity, density, and boiling point. Table 1 labels the silica-titania catalysts and biodiesel products.

Table 1. Labels of catalysts and biodiesel products

Calcination time (h)	Label of catalyst sample	Labels of catalyst products	
		Bimoli palm oil	Bulk cooking oil
6	ST-6h	BPO-6h	BCO-6h
7	ST-7h	BPO-7h	BCO-7h
8	ST-8h	BPO-8h	BCO-8h

3 Results and discussion

3.1 The physicochemical properties silica-titania catalyst

The physicochemical properties of silica-titania catalysts were studied and characterized using FTIR dan DR UV-Vis. This two instruments can inform about the framework of titanium tetrahedral formed in silica-titania catalyst using solid state method.

Fig. 1 shows the FTIR spectra of silica-titania series prepared by variation of calcination time from a mixture of solid silica and titania. The FTIR spectra were scanned at wave number of 1500 – 400 cm-1, a specific area for chemical bonds in silica-titania. Fig. 1 shows very weak band absorption of Si-O-Ti in the vicinity of 960 cm^{-1}. This evidence shows that there is titanium tetrahedral framework in silica-titania sample, however, the fraction of titanium tetrahedral framework cannot be determined from FTIR absorption band due to very weak vibration frequency. The evidence of titanium tetrahedral framework can be confirmed from deconvolution of DR UV-Vis spectra [6].

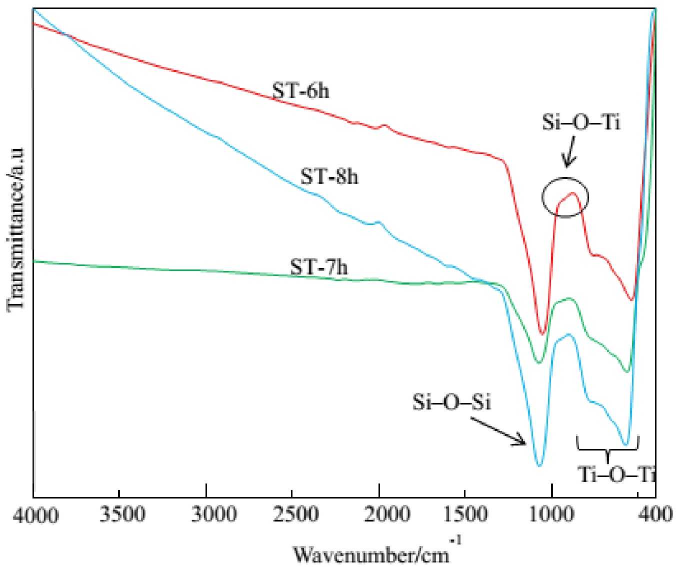

Figure.1. FTIR spectra of silica-titania catalyst prepared by sol gel method using variation of calcination time.

The absorption band of Si-O-Si in silica has strong intensity with broaden peak at wave number around 1200-1000 cm^{-1}. At wave number around 800-600 cm^{-1}, the absorption band of Ti-O-Ti bond in un-reacted TiO_2 also shows strong absorption with boaden band. The existence of absorption bands of Si-O-Si and Ti-O-Ti bonds show that not all silica reacted with titania and formed silica-titania through Si-O-Ti bond [6]–[8]. Fig. 2 shows the DR UV-Vis spectra of silica titania after deconvolution with Gaussian equation. The peaks of Dr UV-Vis deconvolution are as follows: 210, 240, 270, 305, 335, and 395 nm with absorption band of titanium tetrahedral fraction at wavelength ≤ 270 nm and that of octahedral at 280-400 nm. The results of deconvolution calculation are shown in Table 2.

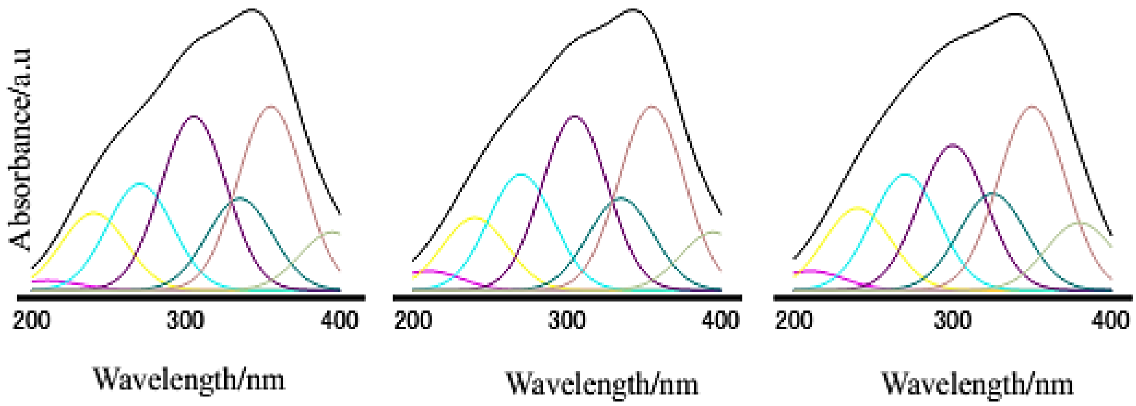

Figure. 2 The spectra of deconvolution of silica-titania catalyst

As shown in Table 2, the titanium tetrahedral fraction is increased with increasing time of calcination from 6h to 8h. The spectra DR UV-Vis deconvolution shows an increasing of titanium tetrahedral fraction in synthetic silica-titania compared to that in pure titania. The enhancement of titanium tetrahedral fraction is due to chemical interaction between silica and titania at temperature that produced Si-O-Ti bond. This evidence is in agreement with data interpretation of FTIR. However, this result is much lower than that reported by sol gel method [5].

Table 2. Fraction of titanium tetrahedral framework in synthetic silica-titania

Time of calcination (h)	Label of catalyst	titanium tetrahedral fraction (%)
6	ST-6h	37.96
7	ST-7h	38.28
8	ST-8h	40.50

3.2 Application of synthetic silica-titania in biodiesel production

The synthetic silica-titania prepared based on variation of calcination time is applied for biodiesel production from 4 types of oils, i.e. Bimoli palm oil, Bimoli waste cooking oil, bulk cooking oil, and waste of bulk cooking oil. The results are shown in Table 3.

In general, silica-titania catalysts prepared by reaction between solids of SiO_2 and TiO_2 using variation of calcination time give effects on the quality of biodiesel products. Higher titanium tetrahedral fraction in synthetic silica-titania catalyst yielded better quality of biodiesel products. As already known, vegetable oil and waste cooking oil cannot be used directly as fuel material due to their high viscosity. Therefore, the viscosity of plant oil and waste cooking oil can be reduced by reacted them with short chain alcohol. The investigation shows that viscosity and density are reduced with increasing fraction of titanium tetrahedral [9].

Table 3. Physical properties of biodiesel yielded from 4 types of selected oil.

Oil Source	Titanium tetrahedral fraction (%)	Biodiesel	Physical properties		
			Density (g/ml)	Viscocity (ml/s)	Acid Number (%)
Bimoli palm Oil	37,96	BPO-6h	0.87626	18.400	0.561
	38,28	BPO-7h	0.87574	18.140	0.561
	40,50	BPO-8h	0.86335	16.380	0.561
Bulk cooking oil	37,96	BCO-6h	0.88078	26.230	0.617
	38,28	BCO-6h	0.87950	20.010	0.561
	40,50	BCO-6h	0.87447	14.250	0.337

With regard to examination of acid number, the biodiesel product is in standard range lower than 0.8. The acid number in waste oil can be reduced with higher fraction of titanium tetrahedral. This evidence has proved that synthetic silica-titania with titanium tetrahedral framework may convert oil with high FFA (free fatty acid) as shown that by using acid catalyst. Based on literature, the formation of titanium tetrahedral framework causes increasing of Bronsted acid in silica-titania catalyst [10], and therefore, as already proved by this study the synthetic silica-titania catalyst may convert oil to biodiesel.

4. Conclusion

The silica-titania catalyst can be synthesized by solid state method using solid precursors applying variation of calcination time. Although the titanium tetrahedral fraction was obtained lower than 50%, however, the synthetic silica-titania catalyst can be able to produce biodiesel from selected oils with its tolerable physical properties in standard range.

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References

[1] C. Berlini, G. Ferraris, M. Guidotti, G. Moretti, R. Psaro, and N. Ravasio, “A comparison between [Ti]-MCM-41 and amorphous mesoporous s ilica silica-titanica as catalysts for the epoxidation of bulky unsaturated alcohols,” *Microporous Mesoporous Mater.*, vol. 44–45, pp. 595–602, 2001.

[2] U. K. Nizar, J. Efendi, L. Yuliati, D. Gustiono, and H. Nur, “A new way to control the coordination of titanium (IV) in the sol-gel synthesis of broom fibers-like mesoporous alkyl silica-titania catalyst through addition of water,” *Chem. Eng. J.*, vol. 222, pp. 23–31, 2013.

[3] U. K. Nizar *et al.*, “The Effect of Titanium Tetrahedral Coordination of Silica-Titania Catalyst on the Physical Properties of Biodiesel,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 335, no. 1, 2018.

[4] U. Kalmar, Y. Manan, R. Sari, R. Sundari, A. Putra, and L. Dj, “The Correlation of Biodiesel Physical Properties and Titanium Tetrahedral Coordination in Silica-Titania

Prepared by Different Moles Ratio of Titania Precursors," *Int. Conf. Chem. Eng. Agroindustry*, 2018.

[5] U. K. Nizar, J. Efendi, L. Yuliati, D. Gustiono, and H. Nur, "A new way to control the coordination of titanium (IV) in the sol-gel synthesis of broom fibers-like mesoporous alkyl silica-titania catalyst through addition of water," *Chem. Eng. J.*, vol. 222, pp. 23–31, 2013.

[6] A. Bhaumik, S. Samanta, and N. K. Mal, "Highly active disordered extra large pore titanium silicate," *Microporous Mesoporous Mater.*, vol. 68, no. 1–3, pp. 29–35, 2004.

[7] D. J. Londeree, "Silica-Titania composites for water treatment," *Univ. Florida*, vol. 53, p. 62, 2002.

[8] T. Kimura, M. Suzuki, M. Maeda, and S. Tomura, "Water adsorption behavior of ordered mesoporous silicas modified with an organosilane composed of hydrophobic alkyl chain and hydrophilic polyethylene oxide groups," *Microporous Mesoporous Mater.*, vol. 95, no. 1–3, pp. 213–219, 2006.

[9] S. M. Coman and V. I. Parvulescu, "Heterogeneous Catalysis for Biodiesel Production," *Role Catal. Sustain. Prod. Bio-Fuels Bio-Chemicals*, pp. 93–136, 2013.

[10] G. N. Shao, R. Sheikh, A. Hilonga, J. E. Lee, Y. H. Park, and H. T. Kim, "Biodiesel production by sulfated mesoporous titania-silica catalysts synthesized by the sol-gel process from less expensive precursors," *Chem. Eng. J.*, vol. 215–216, pp. 600–607, 2013.