

ZSM-5 for the synthesis of Li_4SiO_4 for biodiesel production catalyst

Yu-Yan Chen^a, Yong-Ming Dai^a, Chiing-Chang Chen^{a,*}

^aDepartment of Science Application and Dissemination, National Taichung University of Education, Taichung, Taiwan

*Email: ccchen@mail.ntcu.edu.tw

Abstract

Using biodiesel for replacing petrodiesel has become the most popular issue in recent years. The purpose of bioresource development is to ease the petroleum exhaustion problem. This study synthesizes biodiesel from soybean oil using transesterification over a lithium orthosilicate (Li_4SiO_4) catalyst. The catalyst is prepared using a simple solid-state reaction, mixing and grinding ZSM-5 with Li_2CO_3 calcined at 800 °C in air for 4 h. Under the optimal reaction conditions of methanol/oil molar ratio 12:1, 6 % (wt/wt oil) catalyst amount, and a reaction temperature 65°C for 2 h, there is a 97.2 % conversion to biodiesel from soybean oil. The present study also evaluates the effects of methanol/oil ratio, catalyst amount, and reaction time on the conversion. The catalysts are characterized by Scanning electron-microscopy (SEM-EDS), Thermogravimetric analysis (TGA), BET surface area measurements and Hammett indicator method.

Keywords: Lithium Orthosilicate (Li_4SiO_4), Biodiesel, Transesterification, ZSM-5

NSC Project no.: NSC 102-2622-M-142-001

1 Introduction

There is a great interest in the development of renewable fuel due to the growing concerns about atmospheric pollution, global warming, and limited availability of traditional fossil fuels. Under the effect of energy crisis, biomass energy with the strengths of recyclability and low pollution is regarded as the

potential substitute for petroleum to release energy crisis [1-3]. The transesterification process is also called alcoholysis because the ester reacts with a short-chain alcohol. Conventional processes of biodiesel production involve in using catalysts under mild temperatures (60–80°C) and atmospheric pressure. The transformation between fatty acids contained in vegetable oil (e.g., rapeseed, sunflower, or soybean oil) and low-molecular weight alcohol (methanol) could form the alkyl ester of fatty acids such as FAME. This reaction is useful for the biodiesel production. However, the presence of a catalyst (a strong acid or a base) considerably accelerates the adjustment of the equilibrium process. The overall process consists of consecutive and reversible reactions, in which di- and monoglycerides form as the intermediates and alkyl ester as the final product. There are four principal approaches to the synthesis of biodiesel involving in the transesterification of the triglycerides of plant oil and animal fat, including base catalysis, acid catalysis, employing supercritical alcohol conditions and enzyme catalysis [4, 5]. The current employed commercial processes of biodiesel rely on the transesterification catalyzed by homogeneous alkaline catalysts (NaOH or KOH dissolved in methanol, a corrosive liquid) [6, 7]. However, there are several difficulties in this reaction. The catalysts cannot be recovered, must be neutralized, and cannot be reused, and the separation of fatty acid methyl ester (FAME) from the catalyst during the process also generates large volumes of wastewater. This results in the loss of useful materials and produces large quantities of water since the purification of the ester phase is subsequently necessary. The use of

heterogeneous solid catalysts could be an attractive solution to overcome these disadvantages. Heterogeneous solid base catalysts have several advantages such as ease of catalyst separation, recyclability, eco-friendliness and environmental benignity [8].

ZSM-5 is used in various catalytic applications due to the unique combination of properties such as hydrothermal stability, well-defined micro-porosity and acidity; however, their catalytic applicability is restricted due to diffusional limitations for bulk molecules [9-11]. The diffusional constraints can be minimized by a controlled formation of intra-crystalline mesopore system. The experiments in this study used ZSM-5 as a material for preparing solid base catalysts using Li_2CO_3 as an activating agent through a solid state reaction. The catalyst is air-insensitive and can be directly used for the biodiesel production without further drying or thermal pretreatment. This approach controlled extraction of framework silicon in alkaline medium, referred to as desilication post-treatment, has resulted in a promising and efficient methodology to produce extended mesoporosity in ZSM-5. This combination of the use of Li_2CO_3 on desilicated ZSM-5 can be an efficient robust catalyst.

2 Experimental

2.1 Materials and Preparation of the Catalyst

Soybean cooking oil (Great Wall Enterprise Co., Taiwan), methanol (ACS grade, ECHO Chemical Co., Miaoli, Taiwan), and reagent grade Li_2CO_3 (Shimakyu's Pure Chemicals, Osaka, Japan) were used as received.

The catalyst was prepared by solid-state reaction. A 0.1mole amorphous ZSM-5 powder was added to an aqueous solution containing 0.4 mole Li_2O_3 (Katayama Chemical Co., Japan). The as-prepared solution was dried at 120°C for 24h. Finally, the SiO_2 and Li_2CO_3 mixing powder was well ground and calcined at 900° C in air for 4 h.

2.2 Transesterification reaction procedure

The conversion of soybean oil to biodiesel was performed in a 250 ml flat-bottomed flask, equipped with a reflux condenser and a magnetic stirrer. The effects of the

molar ratio of methanol to oil (3:1-30:1) and catalyst/oil weight ratio (1-7 wt. %) on the conversion of triglycerides to biodiesel were investigated. All of the experiments were performed at atmospheric pressure. After the transesterification reaction, DI water was added into the reaction mixture to stop the reaction. A supernatant was filtered through a common filter paper, and then excess methanol and water were evaporated prior to the fatty acid methyl ester (FAME) analysis.

2.3 Instruments and analytical methods

The base strength of the as-prepared catalyst (H_-) was determined using Hammett indicators. 2 h were allowed to elapse for reaching the equilibrium after which no additional color change took place. The characterization of the as-prepared catalysts was performed using a powder X-ray diffractometer (XRD, MAC MXP18, Tokyo, Japan), with $\text{Cu K}\alpha$ radiation, over a 2θ range from 20 to 80°, with a step size of 0.04°, and at a scanning speed 3° min⁻¹. The FAME concentration, expressed as the biodiesel purity of the product, was determined using a gas chromatography system (Thermo trace GC ultra, Thermo Co., Austin, Texas, USA), equipped with a flame ionization detector, a capillary column (Tr-biodiesel (F), Thermo Co., 30 m in length with 0.25 mm i.d. and 0.25 μm film thickness), the programmed column oven, and a programmed temperature injector. The oven temperature program consisted of starting at 120 °C (hold 1 min), increasing at a rate of 30 °C min⁻¹ to 220 °C (hold 1 min), and then increasing at a rate of 10 °C min⁻¹ to 250 °C (hold 1 min). The temperature of the programmed 3 injectors was 90 °C for 0.05 min, and programmed to 260 °C at a rate of 10 °C min⁻¹. Nitrogen was used as a carrier gas with a flow-rate of 2 ml min⁻¹. The amount of FAME was calculated using the internal standard (methyl heptadecanoate) method, according to method CNS 15051.

3 Results and Discussion

3.1 Characterizations of as-prepared catalysts

Figure 1 shows the XRD patterns of ZSM-5 samples, all of which agree well with those of highly crystalline zeolite ZSM-5. Li_4SiO_4 shows very low crystallinity, almost amorphous morphology. This phenomenon indicates that the further aggregation of nano-particles

into zeolite crystal. The XRD patterns of samples depicted 1 exhibit a doublet at $2\theta = 6-10$ along with a triplet at $2\theta = 22-25$ representing the ZSM-5 framework structure. The XRD patterns of prepared Li_4SiO_4 under different Li_2CO_3 / ZSM-5 mole ratio. Irrespective of the different extent of Li_2CO_3 loading, no change in percentage crystallinity of ZSM-5 and no additional peak of Li_4SiO_4 are observed in the XRD pattern. This indicates uniform distribution of Li_4SiO_4 over ZSM-5 catalyst support.

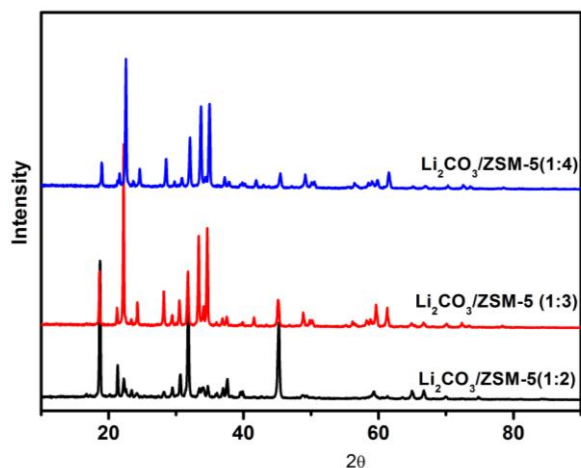


Figure 1 The XRD patterns of ZSM-5, Li_2CO_3 and as-prepared catalyst.

Figure 2 (a) presents FE-SEM images of the waste silicone being converted into $\text{Li}_2\text{CO}_3/\text{ZSM-5}$ powder and the chemical composition of the $\text{Li}_2\text{CO}_3/\text{ZSM-5}$ powder determined by EDS. The FE-SEM micrograph of the $\text{Li}_2\text{CO}_3/\text{ZSM-5}$ powder indicates that the surface is spherical and impermeably porous in nature. Elemental composition with EDS shows that SiO_2 and Al_2O_3 is the main detected component (Figure 3 b). The $\text{Li}_2\text{CO}_3/\text{ZSM-5}$ powder exhibits the type III nitrogen adsorption–desorption isotherm (Figure 3 c). The type III isotherm of LPMSN generally shows prominent adsorption at high relative pressures (P/P_0), indicating the macropore adsorption. The corresponding BET specific surface area is calculated to be $0.283 \text{ m}^2/\text{g}$. The pore size distribution calculated from the BJH method shows a broad pore size ranging in 79 nm (Figure 3 c).

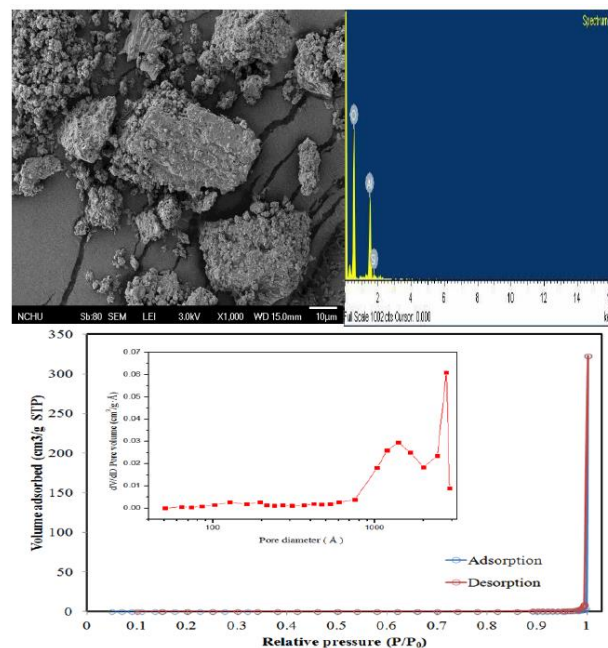
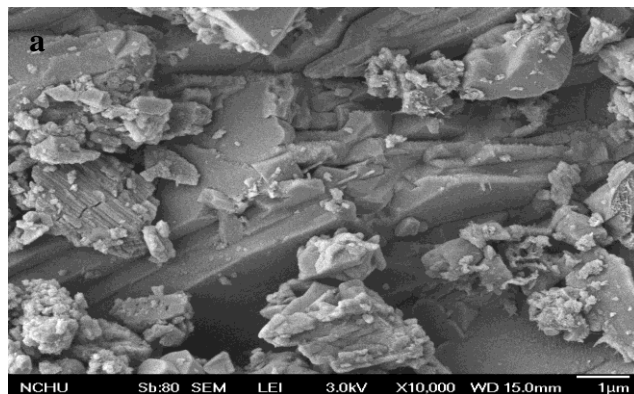


Figure 2 (a) FE-SEM morphology (b) EDS elemental analysis and (c) Nitrogen adsorption–desorption isotherm and pore size distribution of $\text{Li}_2\text{CO}_3/\text{ZSM-5}$ powder.

Catalyst was prepared with grinding ZSM-5 and Li_2CO_3 by the simple solid-state reaction method are shown in **Figure 3**. **Figure 3 (a-c)** shows typical SEM images of the as-prepared catalyst. All catalysts particles have an average grain size of approximately 50-100 μm . Many of the small particles with polyhedral crystals and flake cohered on the surface of catalyst and had impermeable porous surfaces. Then, the catalyst to become form irregular nanoplates above $\text{Li}_2\text{CO}_3/\text{ZSM-5}$ mole ratio 3/1 and the agglomerate nanosheets shape increases with further increasing $\text{Li}_2\text{CO}_3/\text{ZSM-5}$ mole ratio



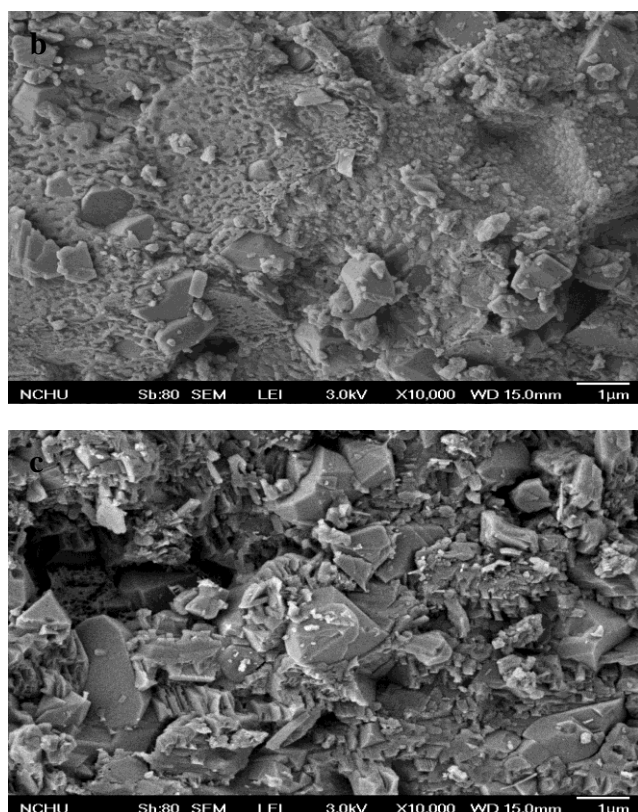


Figure 3 FE-SEM images of as prepared catalyst by the solid state reaction at 800 °C, 4 h; for $\text{Li}_2\text{CO}_3/\text{ZSM}$ molar ratio (a) 2/1 (b) 3/1 (c) 4/1.

3.2 Transesterification reaction condition optimization

The investigated variables include the catalyst amount (g), the methanol/oil ratio (mol/mol), the reaction time (h), and the reaction temperature (°C). The catalyst amount varies in the range of 2-10 wt. %. As shown in **Figure 5**, the conversion increases as the catalyst amount increasing 2-6 wt. %. The conversion reaches a plateau value at the catalyst weight percent between 6 wt. %. Stoichiometrically, the transesterification of soybean oil requires three moles of methanol for each mole of oil. Since transesterification reaction is a reversible reaction, excess methanol would shift the equilibrium towards the direction of FAME formation. As evidenced in the **Figure 5**, when the methanol loading increases, the conversion increases considerably. The maximum conversion ratio is 98.1% at the methanol/oil molar ratio of 12/1.

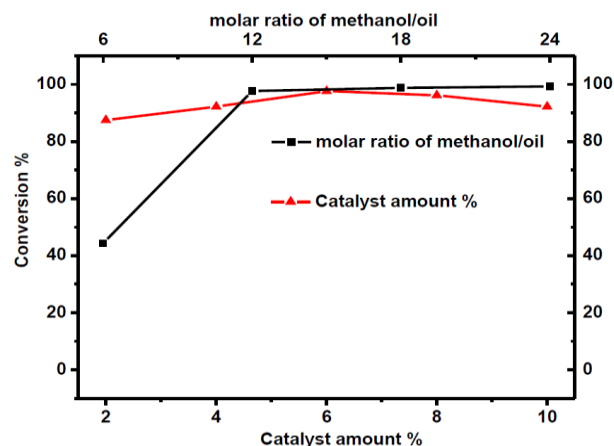


Figure 5 Influence of catalyst amount and methanol/oil molar ratio on the conversion

Figure 6 displays the effects of reaction time on the conversion. The conversion increases steadily within the reaction time range of 1 h, and thereafter remains nearly constant as a result of a nearly equilibrium conversion. Reaction time is an important factor affecting the whole process. That transfer rate increases with time and has a maximum value at 1 hour. Then transfer rate declined obviously, which might be resulted from saponification within long reaction time.

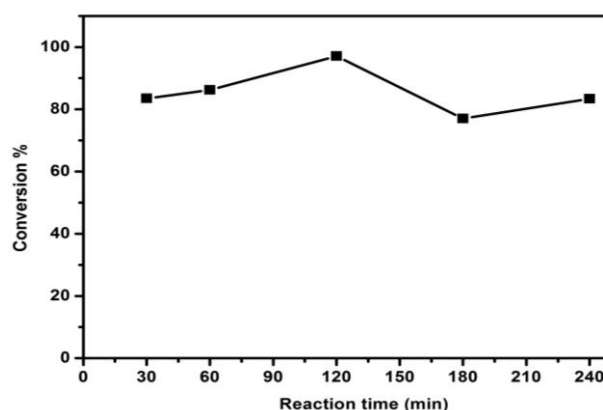


Figure 6 Influence of reaction time and on the conversion.

After the transesterification being completed, the samples are recovered using simple decantation. The remaining catalyst in the reactor is used for catalyzing the next batch of transesterification. As can be seen from **Figure 7**, a biodiesel purity of 72.2% could be obtained even after recycling the catalyst 3 times. Because the amount of catalyst used in the next run is lower than the initial run, it might partly be responsible for the reduced biodiesel purity during the subsequent run.

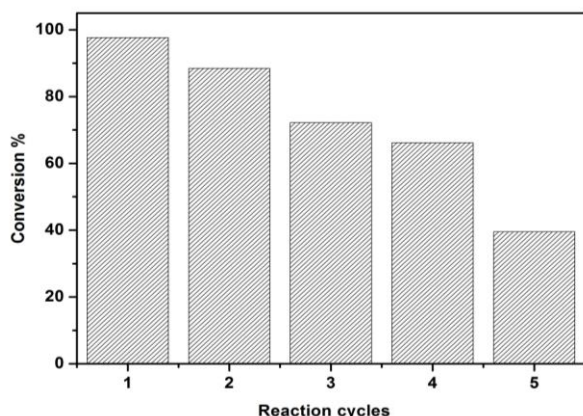


Figure 7 Reusability study after five reaction cycles for catalyst.

4 Conclusions

The method of reusing ZSM-5 to prepare solid catalyst could recycle the waste, minimizing contaminants, reducing the cost of catalyst. Preparation Li_4SiO_4 catalysts with the ZSM-5 were studied and applied to the transesterification of Soybean oil into biodiesel. Several variables of reaction were studied and it was found that the optimum catalyst loading into the reaction media was 6% (w/w). The ratio of 12:1 gave the highest conversion. Also, increasing the reaction time up to 4hr led to the highest level of activity. This biphasic system allows easy separation of products from catalyst and shows good recyclability. In addition, this is one of the best catalytic systems available for biodiesel improvement under the ZSM-5 with lithium carbonate composite.

Acknowledgments

The authors thank NSC Taiwan under the grant of NSC 101-2622-M-142-001 for financially supporting this study.

References

- [1]. S. Tang, L. Wang, Y. Zhang, S. Li, S. Tian, B. Wang. "Study on Preparation of $\text{Ca}/\text{Al}/\text{Fe}_3\text{O}_4$ Magnetic Composite Solid Catalyst and Its Application in Biodiesel Transesterification." *Fuel Processing Technology*, 95, pp.84-9, 2012.
- [2]. M.D. Kaur, A.J. Ali. "Lithium ion impregnated calcium oxide as nano catalyst for the biodiesel production from karanja and jatropha oils." *Renewable Energy*, 36, pp.2866-71, 2011.
- [3]. M.D. Kaur, A.J. Ali. "Nanocrystalline Lithium Ion Impregnated Calcium Oxide As Heterogeneous catalyst for Transesterification of High Moisture Containing Cotton Seed Oil." *Energy Fuels*, 24, pp. 2091-7, 2010.
- [4]. K.T. Chen, J. X. Wang, Y. M. Dai, P. H. Wang, Cyong-Ying Liou, Chia-Wei Nien, Jhong-Syuan Wu, Chiing-Chang Chen, "Rice husk ash as a catalyst precursor for biodiesel production", *Journal of the Taiwan Institute of Chemical Engineers*, 44(4), pp. 622-629, 2013.
- [5]. Y.M. Dai, K.T. Chen, C. C. Chen. "Biodiesel Production from Microalgae Oil Catalyzed Using Solid Catalysts", *Chemical Engineering Journal*, 250(2), pp. 267-273, 2014
- [6]. S. H. Wang, Y.B. Wang, Y.M. Dai, J.M. Jehng. "Preparation and characterization of hydrotalcite-like compounds containing transition metal as a solid base catalyst for transesterification." *Applied Catalysis A: General*, 439-440, pp. 135-141, 2012.
- [7]. M. K. Lam, K. T. Lee. "Catalytic transesterification of high viscosity crude microalgae lipid to biodiesel: Effect of co-solvent." *Fuel Processing Technology* 110, pp. 242-248, 2013.
- [8]. M. Fan, P. Zhang, Q. Ma. "Enhancement of Biodiesel Synthesis from Soybean Oil by Potassium Fluoride Modification of a Calcium Magnesium Oxides Catalyst." *Bioresource Technology*, 104, pp.447-50, 2012.
- [9]. Z.T. Xue, T. Zhang, J.H. Ma, H.X. Miao, W.M. Fan, Y.Y. Zhang, R.F. Li. "Accessibility and catalysis of acidic sites in hierarchical ZSM-5 prepared by silanization." *Microporous and Mesoporous Materials*, 151, pp. 271-276, 2012.
- [10]. V. Grieken, J.L. Sotelo, J.M. Menendez, J.A. Melero. "Anomalous crystallization mechanism in the synthesis of nanocrystalline ZSM-5." *Microporous and Mesoporous Materials*, 39, pp. 135-47, 2000.
- [11]. M. Singh, R. Kamble, N. Viswanadham. "Effect of crystal size on physico-chemical properties of ZSM-5." *Catalyst Letter*, 120, pp. 288-93, 2008.