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High-silica zeolite beta as a heterogeneous catalyst in transesterification of triolein for biodiesel production

Yu-Yuan Wang, Bing-Hung Chen*

Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT

Zeolite beta with a high Si/Al ratio as a heterogeneous catalyst in the transesterification of triolein for biodiesel production was synthesized hydrothermally in fluoride media. The prepared zeolite beta was subsequently treated with dilute NaOH solutions to render better catalysis in the transesterification reaction. Effects of heating procedures, namely reflux and microwave heating, to the reaction system and sizes of the zeolite beta particles on the conversion of triolein to biodiesel were investigated as well. A conversion efficiency over 90% could be attained within an hour of the reflux reaction. Moreover, these Na-treated zeolite catalysts still exhibit acceptable durability and good catalysis in the transesterification reaction after nine consecutive cycles. It is inferred that sodium cations existing in the cages and the defect sites of the NaOH-treated zeolite beta can be supplied to the surface of the catalysts during the transesterification reaction and, thus, to enhance the catalysis.

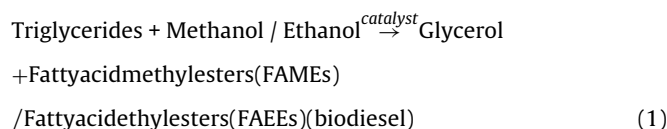
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1. Introduction

The global demand in energy has risen sharply owing to the rapid industrialization and the improved quality of life. Moreover, the excessive emission of anthropogenic carbon dioxide associated with the utilization and extraction of the energy to meet the rapidly growing demand has given rise to the global warming and severe weather changes, threatening the future of the mankind. Consequently, the relentless pursuit of alternative and renewable energies to alleviate these problems are attempted by many scientists and engineers all around the world [1–4]. Out of various renewable energy resources, biodiesel has drawn more attention, as it is produced from renewable biological sources and no significant alteration on regular diesel engines is required with biodiesel or its blends with petro-diesel as the fuel [1]. Moreover, the diesel engines fueled with biodiesel and its blends generally emit less pollutants, e.g. less soot and CO in the exhaust [1], and, thus, become the main powertrains to the public transport or the urban buses.

Biodiesel, a mixture of fatty acid alkyl esters, is usually produced by esterification or transesterification of vegetable oils or animal fats with methanol or ethanol in the presence of suitable catalysts

[2–7]. In general, methanol is more popular than ethanol as the source of the short-chain alcohol in the transesterification reaction. The general equation of the transesterification reaction can be expressed as follows:



To achieve a higher production yield of biodiesel, the transesterification reaction of triglycerides was often conducted at a temperature closed to the boiling point of methanol by the reflux heating. However, in recent years, an alternative heating method, i.e. the microwave irradiation, has been proposed and used in the transesterification reactions [8–11]. When the reaction is carried out under the microwave heating, the transesterification can be efficiently accelerated [8–12].

Microwave is a form of electromagnetic radiation with a frequency between 300 MHz and 300 GHz. Coincidentally, the energy levels associated with the dipolar interaction and ionic induction are in the range of the microwaves. Hence, polar materials such as alcohol and triglycerides can absorb the microwave irradiation and, thus, be excited [8]. Microwave irradiation can provide a faster heat-transfer to the targets, compared with conventional heating

* Corresponding author.

E-mail addresses: bhchen@alumni.rice.edu, bkchen@mail.ncku.edu.tw (B.-H. Chen).

method [8]. Therefore, it is possible to perform the reactions more quickly and efficiently with the microwave reactors. Therefore, it is one aim of this work to study the influence of the different heating methods on the efficiency of the transesterification reaction.

Nowadays, homogenous alkali catalysts are commonly used in the transesterification reaction. They provide rapid conversion of triglycerides to biodiesel, however, the saponification between fatty acids and alkali cations and the high costs in the subsequent purification of biodiesel, for example, removal of the homogenous alkali catalyst, have made this process less competitive and uneconomic. Alternatively, heterogeneous catalysts suitable for the transesterification reaction of triglycerides have been extensively studied in these days [2–7,13,14]. For instance, zeolites modified by alkali cation or metallic polyacids such as tungstophosphoric acid (TPA) have emerged as interesting solid bases [13,14].

Zeolites are microporous aluminosilicate minerals [15]. In particular, they possess uniform mesopores and micropores that can be used as selective catalysts, adsorbents and ion-exchange beds in water purification owing to their specific pore characteristics in molecular dimensions [15]. Among various frameworks of zeolites, zeolite beta (often denoted as zeolite BEA) is one of the important active catalysts frequently used in the petrochemical industry. Zeolite beta was first synthesized by the Mobil Research and Development Laboratories in 1967 [16]. It possesses a three-dimensional 12-membered ring channel system with pore diameters of 0.55 nm × 0.55 nm and 0.76 nm × 0.64 nm, and the larger accessible volume of micropores [16].

By the momentous work of Cambor et al. [17–20], zeolite beta with a wide range of Si/Al ratios from 6.5 to infinity can be prepared from the starting gels with fluoride anions. Therefore, efforts concerning its new preparation method and advanced applications are undertaken by many researchers worldwide. For instance, the high-silica zeolite beta contains stable framework, but is weakly resistant to alkali solution [20]. Furthermore, experimental evidences revealed the existence of significant transfer of electrons from F⁻ to the Si atoms in the framework [17], bringing it energetically favorable for alkali ions to interact with the framework Si. Notwithstanding, the alkali post-treatments could possibly give more defects to the framework on the high-Si zeolite beta by the interaction between F⁻ anions and alkali cations, which diminishes the stability of the zeolite framework. In this work, it is our conjecture that the alkali adsorbed or exchanged to zeolites could act as the active catalysts in the transesterification of triglycerides for biodiesel synthesis.

In general, the elementary building units of zeolite are mainly [SiO₄/2]⁻ and [AlO₄/2]⁻ tetrahedra, along with variety of cations, such as Na⁺, K⁺, and Ca²⁺, dwelling in the porous structure of zeolites [15]. Nowadays, synthetic zeolites are commonly prepared with the hydrothermal dissolution-crystallization mechanism. Explicitly, the synthesis of zeolite is carried out at an elevated temperature in the aqueous system containing the silicon compounds, e.g. colloidal or fused silica, aluminum salts such as Al₂O₃, alkali hydroxides like NaOH to assist the dissolution, as well as directing/templating agents and other additives [15,17–23]. Notably, the relatively easier synthesis of zeolitic materials with fine nanometer-sized structure was recently reported with the use of proper templates and a recrystallization method [21,22].

Up to now only few reports on the alkali post-treated zeolites could be found in the open literature [13]. Nevertheless, finding any report on the catalyzed transesterification of triglycerides using the high-Si zeolite beta is even scarcer. Consequently, the main objective of this work is to study the transesterification of triglycerides in excess methanol in the presence of the high-Si zeolite beta catalysts. The effect of the heating methods to the transesterification is also attempted.

2. Experimental

2.1. Materials

Triolein (*aka* glyceryl trioleate, ~65%), *n*-hexane, *n*-heptane, hydrofluoric acid (HF, 48 wt%), tetraethyl ammonium hydroxide (TEAOH, 35 wt%), and tetraethyl orthosilicate (TEOS, 98%) were obtained from Sigma-Aldrich (St. Louis, MO). Sodium hydroxide and anhydrous methanol (HPLC grade) were purchased from Mallinckrodt Baker (Phillipsburg, NJ). All chemicals were of reagent grade and used as received. According to our ¹H NMR analysis, the purity of triolein in terms of triglycerides is greater than 99%. Zeolite beta used in this work was synthesized according to the procedure revised from those reported in the literature [17]. Deionized water from a Millipore Milli-Q ultrapurification system having resistivity greater than 18.2 MΩ cm was used in the sample preparation.

2.2. Synthesis of high-Si zeolite beta (BEA)

Zeolite beta of high silicon content was synthesized hydrothermally at 140 °C. Adequate amounts of TEAOH and TEOS were mixed in deionized water in a plastic vessel at an ambient temperature under stirring to make a clear solution. Subsequently, HF was added dropwise into this clear solution mixture, leading to the formation of the highly viscous solid-like gel. This white gel was transferred into several PTFE-lined stainless steel autoclaves for further hydrothermal crystallization. In brief, the molar compositions of the starting mixtures were given as TEOS/(0.4–0.7) TEAOH/(0.4–0.7) HF/(2–8) H₂O. Notably, no aluminum salt was intentionally added into the reaction system for the synthesis of the zeolite beta in this work.

The hydrothermal synthesis of zeolite beta was carried out statically at 140 °C for 3–12 days. Zeolite BEA of different sizes could be obtained by varying the hydrothermal reaction time and the compositions of the starting mixtures. The resultant solid product was rinsed thoroughly with deionized water, and dried up in the oven at 120 °C for 2 h to remove water on the solid surface and moisture in the intra-pores. Finally the high-Si zeolite beta was obtained by calcination of this solid powder at 538 °C for 8 h in air to remove any residual organic compounds. Notably, to improve the catalysis of the high-Si zeolite BEA in the transesterification reaction of triolein, zeolite beta had to be treated with NaOH_(aq) and transformed into zeolites in Na-form or the amorphous sodium silicates, denoted as Na-BEA.

Na-BEA was attained by the NaOH treatment on the as-obtained zeolite beta. The alkali post-treatment process was performed in 1–2 wt% NaOH solution, i.e. with a mass ratio of Na-to-zeolite BEA from 6 to 10 wt%-eq, at the room temperature for a period up to 27 h. It has to mention that the Na⁺ concentration in the solution used for alkali post-treatment process was given in the equivalent weight-percentage (wt%-eq.) of sodium, based on the mass of zeolite beta initially present in the alkali post-treatment process. Afterwards, the solid product was rinsed with deionized water (10× of zeolite mass) twice at an ambient temperature. Remarkably, the washing process was finished with a duration no less than 20 min to remove weakly adsorbed sodium ions. Subsequently, the Na⁺-ion treated zeolite beta were dried in an oven at 120 °C for 2 h, and calcined at 500 °C for 8 h in air to give the Na form of high-Si zeolite beta or the amorphous sodium silicates (Na-BEA).

For simplicity and concision in this report on the expression of the catalysts used, the denotation of the Na-BEA(*size*, *time*) are used, where *size* stands for the average size, in μm, of the zeolite beta initially used, and *time* for the duration of the alkali post-treatment process in hours.

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