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Optimization of sodium loading on zeolite support for catalyzed transesterification of triolein with methanol

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HIGHLIGHTS

- Na-loaded zeolite HY was used to catalyze transesterification of triolein in CH_3OH to biodiesel.
- The ion-exchange method was utilized to dope Na^+ onto surface of zeolite HY support.
- A high conversion yield of triglycerides to biodiesel at 65 °C was obtained as high as 97.3%.

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ABSTRACT

Optimization of sodium loading on zeolite HY for catalyzed transesterification of triolein in excess methanol to biodiesel was studied. Zeolite HY catalyst was activated by loading sodium ions to their surface via an ion-exchange method. The effects of ion-exchange process parameters, including the temperature, the process time, the pH value, as well as concentrations and sources of Na^+ cations (NaOH, NaCl and Na_2SO_4), on the conversion yield of triolein to biodiesel were investigated. Most of these Na^+-activated zeolite HY catalysts could really facilitate the catalyzed transesterification reaction of triolein to biodiesel at a lower temperature near 65 °C. Consequently, a high conversion yield of triglycerides to biodiesel at 97.3% was obtained at 65 °C. Moreover, the durability of zeolite catalysts was examined as well. Catalytic performance tests of these zeolite catalysts in transesterification did not show a significant decrease in catalysis at least for three batch cycles.

1. Introduction

Depleting reserves of fossil fuels and global environmental concerns resulting from overconsumption of fossil fuels have prompted an urgent demand for alternative fuels (Atadashi et al., 2011; Leung et al., 2010; Ma and Hanna, 1999; Sharma et al., 2011). Development of environmentally benign alternative energies to reduce the reliance on non-renewable fossil resources is of an indispensable action. Therefore, biodiesel has becomes a focus of alternative energy researches in recent years (Atadashi et al., 2011; Leung et al., 2010; Ma and Hanna, 1999; Sharma et al., 2011; Vicente et al., 2007).

Biodiesel comprises of a mixture of long-chain fatty acid methyl esters (FAMEs) or ethyl esters (FAEEs) commonly produced from vegetable oils or animal fats (Barnwal and Sharma, 2005; Lee et al., 2007; Ma and Hanna, 1999). With a similar range of hydrocarbon chains as petrodiesel, biodiesel can be used alone or as a blend with petrodiesel for diesel-powered vehicles. Moreover, it has been reported that the use of the mixed biodiesel–petrodiesel fuel could effectively reduce emission levels of common environmental pollutants such as soot, carbon monoxide, and hydrocarbons from diesel-powered vehicles (Bluhm et al., 2012; Panwara et al., 2011). Hence, biodiesel has been generally considered as an environmentally friendly alternative energy and one promising remedy to alleviate the aforementioned severe environmental issues stemmed from the overconsumption of unsustainable fossil fuels (Atadashi et al., 2011; Semwal et al., 2011).

Biodiesel is fabricated mostly from the transesterification of triglycerides of biological origins in excess methanol in presence of suitable catalysts (Ma and Hanna, 1999; Macario et al., 2010; Wang et al., 2012). The general equation of the transesterification reaction can be expressed as follows:

$$\begin{aligned}&\text{Triglycerides} + \text{Methanol}/\text{Ethanol} \xrightarrow{\text{catalyst}} \text{Glycerol}\\&+ \text{Fatty acid methyl esters (FAMEs)}/\text{Fatty acid ethyl esters (FAEEs)}\\&\times (\text{biodiesel})\end{aligned} \tag{1}$$

In general, methanol or ethanol in excess is utilized in the transesterification reaction to drive the reaction equilibrium further to the product side, namely in favor of more biodiesel

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produced. Besides, catalysts are present to facilitate the transesterification of triglycerides and, thus, to promote biodiesel production. Both homogeneous (Leung et al., 2010; Macario et al., 2010) and heterogeneous catalysts (Atadashi et al., 2011; Camara and Aranda, 2011; Del Romedio Hernández et al., 2010; Kim et al., 2008; Macario et al., 2010; Sankaranarayanan et al., 2012; Semwal et al., 2011; Srilatha et al., 2012) have been successfully applied to catalyze the transesterification of triglycerides with methanol and ethanol for biodiesel production. However, homogeneous catalysts, e.g. sulfuric acid and sodium hydroxide, give not only faster reaction rates, but also some drawbacks such as the corrosion of a reactor by sulfuric acid and a need of an additional cost to purify biodiesel products (Atadashi et al., 2011; Ma and Hanna, 1999). Therefore, heterogeneous (solid) catalysts have been preferably adopted in biodiesel production to avoid disadvantages associated with the use of homogeneous ones (Atadashi et al., 2011; Ma and Hanna, 1999; Semwal et al., 2011).

Zeolites are microporous aluminosilicate minerals and are well known for their catalysis in various industrial processes, for example, the fluid catalytic cracking (FCC) of heavy petroleum distillates, and the octane number enhancement of light gasoline by isomerization (Weitkamp, 2000). Zeolites could be found in nature and synthesized in large scale industrially. In general, zeolites in the pristine form are solid acids (Weitkamp, 2000). Nonetheless, zeolites modified by the ion-exchange process with alkali cations or by decomposition of an occluded alkali metal salt have emerged as interesting solid bases (Davis et al., 2000; Hattori, 1995; Philippou and Anderson, 2000; Philippou et al., 1999). They could catalyze reactions that require a base site, and the base strength of the alkali ion-exchanged zeolite increases with increasing electropositivity of the exchanged cation. However, not until very recently have zeolites been attempted in biodiesel production from either esterification of fatty acids or transesterification of oils with short-chain alcohols, e.g. methanol. As a result, zeolites have been successfully demonstrated in the catalyzed transesterification of triglycerides for biodiesel production (Brito et al., 2007; Noiroj et al., 2009; Ramos et al., 2008; Suppes et al., 2004; Wang et al., 2012; Xie et al., 2007). For example, sodium was successfully doped via an ion-exchange method to zeolites and mesoporous silicate supports, such as zeolite HY and MCM-22, showing significant catalytic improvements in the transesterification and the durability of catalysts for biodiesel production (Wang et al., 2012). However, details on zeolite modification by a sodium ion-exchange process are still lack and yet to be scientifically explored, even though the catalytic performance of these Na-loaded zeolites was satisfactory.

In this work, we mainly focus on the optimization of the sodium ion-exchange process to zeolites for the improved catalysis and durability to transesterification of triolein with methanol in excess. Process parameters, for example the pH value, the temperature and the process duration, as well as effect of different sodium sources, were studied in an attempt to shed light on the better advancements of biodiesel production from catalyzed transesterification of renewable vegetable oils.

2. Experiment

2.1. Materials

Triolein (technical grade, ~65%), *n*-hexane, *n*-heptane and methyl oleate were obtained from Fluka–Sigma–Aldrich (St. Louis, MO). Sodium hydroxide, anhydrous sodium sulfate, sodium chloride, ammonium hydroxide solution, and anhydrous methanol (HPLC grade) were purchased from Mallinckrodt Baker, Inc. (Phillipsburg, NJ). Zeolite HY (CBV 780, Si/Al = 80, BET surface area = 780 m^2/g) was supplied from Zeolyst (Conshohocken, PA) in powder form (1–2 μm diameter crystals). All chemicals were of reagent grade and used as received. Deionized water from a Millipore Milli-Q ultrapurification system having resistivity greater than 18.2 MΩ cm was used in this study.

2.2. Modification of the catalysts

Zeolite HY (CBV 780) powder was used as the catalyst support. Detailed procedures to dope sodium onto the zeolite HY surface by ion-exchange methods were given previously (Wang et al., 2012). Briefly, these zeolite HY powder was firstly dehydroxylated at 120 °C overnight and, subsequently, soaked in Na^+ containing solutions (10× catalyst mass) for a certain period. To avoid avalanche of sodium ions leached off from the Na^+ ion-exchanged zeolite HY catalyst during the course of transesterification, these Na^+-treated zeolite samples were rinsed thoroughly with deionized water (10× catalyst mass) twice at ambient temperature to remove any undoped sodium and other impurity. Notably, the rinsing process was finished with a duration no less than 20 min to remove weakly ion-exchanged sodium ions.

Subsequently, these Na^+-treated zeolite catalysts were dried in an oven at 120 °C, and calcined 500 °C in air for 8 h. In this text, the Na^+-treated zeolite HY were denoted as the zeolite NaY. Furthermore, it has to mention that the Na^+ contents in solution used for the sodium ion-exchange process are expressed in the equivalent weight-percentage (wt.%-eq.) of sodium, based on the mass of zeolite HY support initially present in the sodium ion-exchange process.

2.3. Transesterification reaction (biodiesel production)

Triolein, *aka* glyceryl trioleate, was selected as a model oil in this work, because it is one of the most abundant triglycerides in vegetable oils. Though triolein used in this work was reported to be of ca. 65% in purity by the supplier, its purity was more than 99% in terms of triglycerides, according to the ^1H NMR analysis.

Transesterification of triolein in excess methanol to produce methyl oleate as biodiesel was performed in a batch reactor, namely a 250 mL round three-necked Pyrex flask, equipped with a thermometer, a reflux condenser, and a drop funnel. Methanol and zeolite NaY catalyst were pre-heated up close to the boiling point of methanol near 65 °C in the batch reactor before the introduction of triolein that was separately heated to 65 °C as well. This reactor vessel was placed in a constant-temperature water bath over a magnetic stirrer/hot plate (Schott SLR, Mainz, Germany), which could provide a good temperature control within 1 °C. After introduction of triolein, the reaction temperature was always maintained constant at 65 °C. In brief, the transesterification of triolein in excess methanol in presence of various zeolite NaY catalysts was carried out at (1) the initial feed ratio of methanol-to-triolein = 15 by mass, (2) a loading of catalyst-to-triolein = 1 by weight, (3) the reaction temperature at 65 °C, and (4) a constant stirring at 600 rpm.

After reaching a preset reaction time, the reaction was quickly stopped by cooling in an icy bath. The reacting mixture was quickly filtered to separate the solid catalyst. The used zeolite NaY catalysts were also washed with *n*-hexane to remove any adsorbed *as*-synthesized biodiesel. The obtained liquid layer was, subsequently, centrifuged at 4000 rpm for 15 min to ensure the complete separation of the solid catalyst from the biodiesel product. To quantitatively and qualitatively analyze the biodiesel, a GC-FID was utilized. However, the ^1H NMR analysis was also utilized regularly to validate the GC-FID analysis. Prior to the NMR analysis, the decanted liquid layer was transferred to a rotary vacuum evaporator to remove *n*-hexane and any byproducts from the biodiesel layer. Transesterification experiments were conducted in duplicate or triplicate to ensure good empirical reproducibility.