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Low-Al Zeolite Beta as a Heterogeneous Catalyst in Biodiesel Production from Microwave-Assisted Transesterification of Triglycerides

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Abstract

In this work microwave and reflux-assisted transesterification of triolein in methanol was carried out with alkali-loaded low-Al Zeolite Beta as catalyst. The results show that the alkali-treated Zeolite Beta can effectively catalyze transesterification reaction of triglycerides to produce fatty acid ethyl esters (biodiesel), if Zeolite Beta has been properly modified with the alkali ion-exchange process. As a result, the final conversion yield over 90% could be obtained within an hour of reflux reaction. However, the durability of this Na-modified Zeolite Beta still has much room to be improved. In this work, this inferior catalytic durability is overcome by using the low-Al Zeolite Beta with a smaller particle size near 0.5μm. Consequently, for at least eight cycles, cyclic tests of these zeolite catalysts do not result in any significant decrease in catalysis in transesterification reaction. It is inferred that alkali cations existing in defect-sites of low-Al Zeolite Beta can be supplied to the surface of the catalysts during transesterification and enhance the catalysis.

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Keywords: Biodiesel; Transesterification; Microwave reaction; Zeolite Beta; Triglycerides; Ion-exchange.

1. Introduction

Biodiesel, a mixture of fatty acid alkyl esters, is typically produced by esterification or transesterification of vegetable oils or animal fats with methanol or ethanol in presence of suitable catalysts. Commonly, transesterification reaction is employed to convert triglycerides to fatty acid methyl/ethyl esters, which is simply a process of displacement of an alcohol group from an ester by another alcohol. Transesterification can be performed via catalytic or non-catalytic reaction using

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different heating systems [1]. In addition to the conventional reflux heating method, an alternative heating, i.e. microwave irradiation, has been proposed and used in transesterification reactions in recent years. When the reaction is carried out under microwave heating, transesterification is efficiently accelerated in a short reaction time. Consequently, the production of by-products is reduced and a shorter separation time is obtained [1, 2]. Recent researches on transesterification have been focused more on the use of heterogeneous catalysts [1]. For example, zeolites modified by alkali cation exchange have emerged as interesting solid bases [3]. Zeolites are microporous aluminosilicate minerals [4]. In particular, they possess uniform micropores that can be used as selective catalysts and adsorbents owing to their specific pore characteristics in molecular dimensions [4]. Among various zeolites, Zeolite Beta (often denoted by IZA as Zeolite BEA) becomes one of industrially important zeolites, as it contains three-dimensional large pore (12-membered ring) system, larger accessible micropore volume, and easily adjustable Si/Al ratios from 4.5 to infinity. Therefore, a lot of efforts concerning its new preparation method and advanced applications have still been made by several groups. By the momentous work of Camblor *et al.* [5], 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 (F^-). Coincidently, we have discovered that such low-Al Zeolite Beta could efficiently store alkali cations into cages via an ion-exchange process. Until now only few reports are available on sodium ion-exchanged low-Al zeolites. Nevertheless, in the open literature, finding any reports on catalysed transesterification of triglycerides using the low-Al Zeolite Beta is even rare. Therefore, the main objective of this work is to study the transesterification of triglycerides in excess methanol in presence of low-Al Zeolite Beta catalysts.

2. Experiment

2.1 Materials

Triolein (technical grade), n-hexane, n-heptane, hydrogen fluoride (HF, 48 wt%), tetraethyl ammonium hydroxide (TEAOH, 35 wt%), and tetraethyl orthosilicate (TEOS) were obtained from Fluka–Sigma–Aldrich (St. Louis,MO). Sodium hydroxide, and anhydrous methanol (HPLC grade) were purchased from Mallinckrodt Baker, Inc.(Phillipsburg, NJ). Zeolite Beta was synthesized according to the reference [5]. According to our NMR analysis, the purity of triolein in terms of triglycerides is > 99%.

2.2 Synthesis and modification of low-Al Zeolite Beta

An adequate amount of TEAOH and TEOS was mixed in deionized water overnight at room temperature in a plastic vessel under stiring to have a clear solution. Then HF solution was added dropwise, which caused the transformation of the former solution into a highly viscous gel. This white gel was then transferred into several PTFE-lined autoclave reactor vessels. The molar composition of the starting mixture was as follows: SiO_2: 0.4-0.7 TEAOH: 0.4-0.7 HF: 2-8 H_2O.

Crystallization of Zeolite Beta was carried out in static conditions at 140ºC for 3-12 days. The resultant solid product was washed with deionized water and then recovered by filtration. The sample was calcined at 538ºC for 8 h. The Na form of the low-Al Zeolite Beta was obtained by an ion-exchange method using 1-2 wt% NaOH solution (Na-to-solid ratio = 6-10 wt%) at room temperature for 24 h. The solid product was washed thoroughly with deionized water (10× in mass) and then recovered by filtration. The Na/low-Al Zeolite Beta was obtained by calcining at 400 ºC for 8 h. In this study, the low-Al Zeolite Beta supports in two different sizes, 12 μm and 0.5 μm, were synthesized and used in catalyst preparation.

2.3 Transesterification Reaction (Biodiesel Production)

Transesterification reactions were carried out in water bath as a heating system (reflux) and under constant stirring at 700 rpm. The triolein oil, alcohol and catalyst were added respectively to the flask through the condenser. After reaching the expected duration of reaction, the reacting mixture and suitable n-hexane were centrifuged at 5000 rpm for 10 min. The liquid phase at the top was decanted and further extracted with n-hexane. The biodiesel appears in the organic phase as the upper layer, and the glycerin was in the methanol phase as the lower layer. The organic phase layer was transferred to a rotary vacuum evaporator to remove n-hexane. Biodiesel was quantitatively analyzed by a GC-FID and NMR.

The effect of microwave heating in transesterification reaction to the production yield of biodiesel was investigated as well. The experimental conditions used in the reaction is 15:1 (w/w) alcohol to oil and 1:1 (w/w) catalyst to oil. Transesterification reactions were done in presence of Na/catalyst (a loading at 1.93 wt%) at 100ºC. Triolein, methanol and catalyst were added, respectively, into the flask through the condenser, and, then, irradiated at 800 W at 100 ºC for different reaction times.

3. Results and discussion

Fig. 1 and 2. shows the conversion yields of trilein to biodiesel as a function of reaction times. The average particle size of the low-Al Zeolite Beta synthesized was about 12 μm. The Na content on Na/low-Al Zeolite Beta catalyst was about 1.93wt% Na content. Generally, the conversion of triolein to biodiesel could reach more than 90% within an hour in the first two cyclic runs by either reflux (65 ºC) or microwave heating (100 ºC). It is worth mentioning that free sodium was found in the methanol layer, possibly leached out from catalysts used. The content of the leached Na^+ in the methanol layer was equivalent to *ca.* 0.36 wt%, based on the mass of Na/low-Al Zeolite Beta, after the first cycle of the transesterification reaction by reflux.

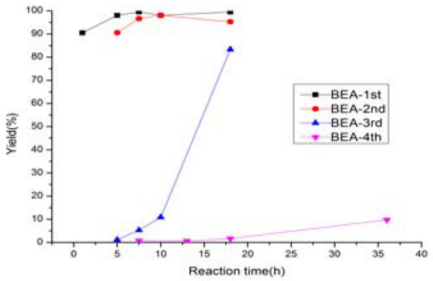

Fig. 1: Yield of methyl esters from cyclic runs of reflux reactions using larger particles of Na/low-Al Zeolite Beta (ion-exchanged with 6%-eq. Na^+).

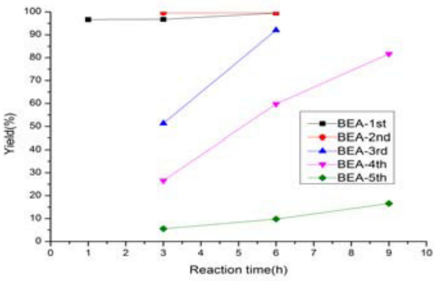

Fig. 2: Yield of methyl esters from cyclic runs of microwave reactions at 100 ºC using larger particles of Na/low-Al Zeolite Beta (ion-exchanged with 6%-eq. Na^+).

Both durability and activity are important indicators of catalysts used in chemical industry. The Na/low-Al Zeolite Beta did not exhibit discernible deactivation in catalysis for the first two cycles of transesterification reaction by reflux heating (Fig. 1). However, in the third cycle, the activity of catalyst obviously declines during transesterification reaction by reflux heating. It would take 18 h to reach 83.3% in biodiesel production yield (Fig. 1). The catalysis of the used Na/low-Al Zeolite Beta after three runs decreased significantly.

Effect of spport sizes, namely low-Al Zeolite Beta, on the resulted conversion efficiency of triolein to biodiesel was studied and attempted. In addition to the larger particles of low-Al Zeolite Beta, the smaller zeolite support with an average size near 0.5 μm was employed. Fig. 3 shows the production yield of biodiesel from triolein using the smaller low-Al Zeolite Beta ion-exchanged with 10%-eq. Na^+. The resulted catalysis in catalyzed transesterification was better that of the larger supports. For example, the conversion yiels could reach more than 90% within three hours during the first fice cyclic runs, and 80% at 8h for the first eight cyclic runs. This significant catalytic improvement in transesterification may be attributable to the smaller particle size but the larger specific area and the probably more exposable cages for the active catalytic species, namely, the sodium cations [6].

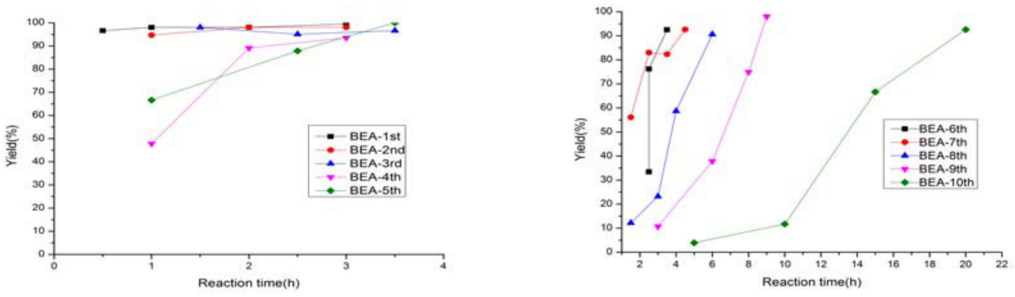

Fig. 3: Yield of methyl esters from cyclic runs of reflux rections using small Na-Zeolite BEA particles (ion-exchanged with 10%-eq Na^+).

4. Conclusion

The Na^+ ion-exchange process successfully modify the low-Al Zeolite Beta asn effective catalyst in transesterification of triolein in excess methanol. In general, the smaller Zeolite Beta support (0.5μm vs. 12μm) gives better catalysis and higher durability. Compared with transesterification of triolein by conventional reflux reaction, the microwave reaction needs a higher reaction temperature than the reflux method. This could be resulted from the poor heating unformity in the microwave reactor that is due to the lack of mechanical stirring. For at least eight cycles of transesterification reaction by reflux method, the Na-Zeolite Beta does not exhibit any significant decrease in catalysis in transesterification of triolein.

Acknowledgements

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