

A SUMMARY OF BIODIESEL PRODUCTION OVER AS-PREPARED CATALYST TRANSFORMED FROM COST-EFFECTIVE CLAYS

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ABSTRACT

This study summarized biodiesel production over *as*-synthesized catalysts transformed from low-cost mineral clays. The porous catalytically materials were obtained by base activation in a simple ways. It was successful to reach high conversion efficiency (*ca.* 95 – 99 %) of transesterification of triglycerides/vegetable oils to fatty methyl acid esters (FAMES) - main components of biodiesel.

Keywords: biodiesel production, triglycerides / vegetable oils, heterogeneous catalyst, FAMES.

1. INTRODUCTION

Overconsumption and negative impacts to environment of fossil fuels have prompted an urgent demand for alternative and environmentally friendly fuels [1, 2]. Biodiesel, a mixture of long-chain fatty acid methyl esters (FAMES) or ethyl esters (FAEEs), is one of renewable energy resources. It is mostly produced by either the esterification of free fatty acids or the transesterification of animal fats, vegetable oils, or even waste frying oils, with short-chain alcohols, typically methanol or ethanol, in presence of suitable catalysts [3 - 6].

There are some disadvantages such as being difficult to separate or purify products, consuming more energy to remove neutralized water from reacted mixture [1, 7] as using homogeneous catalysts in biodiesel production. To overcome these disadvantages, heterogeneous catalysts would be of great interest for biodiesel production [1]. This paper reviews some obtained results of our research group by *as*-synthesized catalysts from natural mineral clays to convert waste vegetable oils to biodiesels [3 - 5, 8, 9]. Methanol was used because of its advantages such as low price compared to other alcohols and physical-chemical properties [10].

2. MATERIALS AND METHODS

2.1. Chemicals

Methyl alcohol anhydrous and palmitic acid (98 %), a product of Sigma-Aldrich[®], were of analytical standard reagent. Vegetable oils were supplied by Uni-President Enterprises Corp. (Tainan, Taiwan) and palm oil produced by Chang Guann Co. Ltd. (Kaohsiung, Taiwan). Natural mineral clays were transformed to solid catalysts by base activation. Then, they were put in a desiccator before transferring to the reactor. 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 the sample preparation.

Raw material was purchased from J.T. Baker Company. Calcined material was obtained by calcination of raw one at 800 °C in 10 h. The calcined material was activated with sodium hydroxide with rate of 1:2 w/w in hydrothermal reactor at 90 °C, followed by calcination at 500 °C for 6 h. The *as*-synthesized catalyst was put in desiccator.

2.2. Equipment and Experiments

The experiments were performed in a vial sealed by a screw-Teflon cap. The reactor was placed in a temperature controlled, and put on a magnetic controlled machine [11].

Firstly, a suitable amount of oils and methanol were separately pre-heated to desired temperature before transferring to the reactor. Consequently, the catalyst was simultaneously added to the reactor. Then, the transesterification reaction was carried out at optimized temperature as well as keep constant of agitation speed. The reaction was quenched by cooling reactor as reaching optimal time. Separated FAMES was analyzed with a GC-FID (Shimadzu GC-2014 with a DB-5 column as 12 m × 0.32 mm × 0.1 μm). All operating conditions were fulfilled by following procedures described in ASTM D6584-08. Finally, the conversion efficiency (Y) of the reaction was calculated by using the relationship mentioned in the previous raw materials [3, 5, 8, 9, 12].

All fresh and recycle *as*-synthesized catalysts were characterized by using various instruments such as XRD, SEM and FT/IR. XRD was performed on Rigaku Ultima diffractometer with Cu K α radiation at 40 kV and 20 mA. A step interval of 0.01° in a 2 θ range of 5° - 50° was set up, with a scanning rate at 10 °/min. Moreover, information in functional groups was recorded via a Jasco FT/IR-400 using the KBr pellet technique in a wavenumber range of 4000-400 cm⁻¹. Furthermore, the morphology was determined by using a scanning electron microscopy (SEM, Jeol JSM-6700F).

3. RESULTS AND DISCUSSION

3.1. Characterization of *as*-prepared catalysts

Characterization of raw, calcined and base-activated kaolin was represented as an example of all our heterogeneous catalysts transformed from mineral clays.

X-Ray diffraction (XRD). The XRD patterns of raw material, calcined material and transformed material were shown in Figure 1. The XRD characteristics of raw material almost disappeared after thermal treatment leading to formation of calcined material (aka metakaolin). Explicitly, disordered metakaolin was formed in this material after dehydroxylation of raw one at 800 °C for 10 h. A new broad band with increasing calcined material ground in 2θ range from 20° to 30°, which is commonly assigned to amorphous phase of SiO₂, could be observed on the XRD pattern of calcined material [13]. The transformed catalyst is quite similar to that of zeolite Linde Type A (LTA, dehydrate form).

Fourier transform infrared spectroscopy (FT-IR). FT-IR analyses were carried out in the range of 4000 - 400 cm⁻¹ to investigate the characteristics of surface chemistry, especially functional groups, on raw, calcined and activated material, Figure 2. It reveals that the feature of raw material (1114.9 cm⁻¹) as well as peak of water absorption disappears during calcination at 800 °C for preparation of calcined material. Once again, significant changes in surface features from calcined material to transformed material in the range 1200 - 400 cm⁻¹ were also observed. Notably, the FTIR spectra of transformed material catalyst before its use in transesterification and transformed material harvested after the fourth batch cycle of transesterification reaction are not obviously discernible.

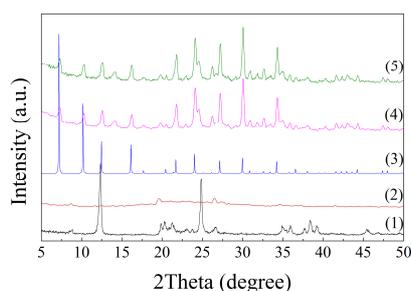


Figure 1. XRD patterns of (1) raw (2) calcined and transformed material [(4) fresh, and (5) recycled one], and (3) dehydrated standard LTA.

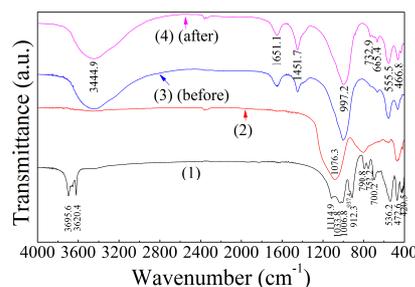


Figure 2. FT-IR spectra of raw (1), calcined (2) and transformed material (3) before and (4) after catalyzing transesterification of vegetable oils in excess methanol.

Scanning Electron Microscopy (SEM). The morphology of raw, calcined and obtained substances was examined with SEM, and their results were exhibited in Figure 3. The raw one mainly consists of stacking of flaky particles with rough surface (Figure 3-left). Despite of being calcined at 800 °C, the morphology of calcined material is insignificantly different from that of its mother. Interestingly, after base-activation treatment, flaky calcined solid turned to cubic material of ca. 2 μm in size (Figure 3-middle).

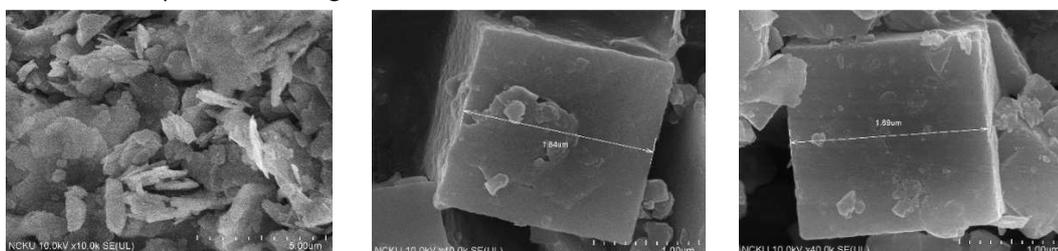


Figure 3. SEM micrographs of parent (left) and base-activated mineral clay [fresh (middle), used (right)].

3.1. Optimization of parameters on the conversion efficiency of triglycerides/vegetable oils to biodiesels

In our point of view, the most important factors were reaction temperature, reaction time, feeding ratio of reactants and catalyst loadings among several factors effect on biodiesel production. Hence, most of our researches were optimized the effects of the significant factors, while others such as agitation speed was kept constant at 600 rpm.

Table 1 reviews optimization conditions of biodiesel production via transesterifying of triglycerides / vegetable oils over as-synthesized catalysts and excess methanol. According to Table 1, ca. 95 – 99 % of triglycerides converted to FAMES under the optimal operating conditions over all the mentioned catalysts.

Furthermore, high conversion efficiency of soybean oils was attained in a shorter durability than that of palm oils because of containing more unsaturated carbon compounds. Moreover, the higher temperature of reaction is, the higher efficiency is. However, experiments were conducted at less than the boiling point of methanol.

Table 1. Optimization conditions of biodiesel production over the as-prepared catalysts synthesized from natural mineral clays.

Reference	Vegetable oils	Catalysts	X ₁	X ₂	X ₃	X ₄	X ₄	Y (%)
Hiep D. T., Chen B. -H [9]	Soybean	Activated clay	2.0	50	20/1	50.0	600	98.7
Wang Y.-Y., Hiệp Đ. T., Chen B.-H., Lee D.-J. [5]	Triolein	Activated MCM-22	5.5	60	15/1	30.0	700	99.0
Hiep D. T., Chen B.-H., Lee D.-J. [3]	Soybean	LTA	1.0	63	20/1	50 - 55	600	97.0
Hiep D. T., Chen B.-H., Lee D.-J. [3]	Palm	LTA	2.0	63	10/1	10	600	95.4

where X₁: Reaction time (h); X₂: Reaction temperature (°C); X₃: Methanol/Oil (wt./wt); X₄: Catalyst loading (wt.%); X₅: agitation speed

3.3. Re-utilization of catalysts

Before using in the next cycle, the used catalysts were washed by using pure methanol. Then, remaining organic substances in/on surface of porous materials were removed by drying at 110 °C for 48 h followed by calcined at 500 °C for 6 h.

In general, there was not any discernible difference in XRD patterns, morphology checked by SEM micrographs and FT-IR spectra between fresh and recycled catalysts, (Figure 1-3). That is, that the structure and morphology of catalyst were still conserved. Besides, performance of catalyst is slightly deteriorated one cycle after one cycle. However, the high conversion efficiency is still attained at least four cycles.

4. CONCLUSIONS

An effective solid catalyst was successfully synthesized from natural mineral clays by simple way of hydrothermal or ion-exchange processes.

Conversion efficiency reached to high values of 95-99 % under optimal conditions of durability of 1-5.5 h, low temperature of 50-63 °C, while feeding ratios and catalyst loadings were in range of 10/1-20/1 and 10-55 %, respectively. In this investigation, activated clay, activated MCM-22, zeolite LTA catalyzed the biodiesel production via transesterification reaction of vegetable oils.

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TÓM TẮT

TỔNG KẾT NGHIÊN CỨU TỔNG HỢP VÀ SỬ DỤNG XÚC TÁC DỊ THỂ CÓ NGỒN GỐC TỪ CÁC KHOÁNG RÊ TIỀN ĐỂ SẢN XUẤT NHIÊN LIỆU SINH HỌC

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Bài báo này tóm tắt các điều kiện tối ưu của quá trình sản xuất nhiên liệu sinh học thông qua phản ứng chuyển đổi ester triglyceride trên nền xúc tác rắn khi có dư methanol. Các xúc tác rẻ tiền, có nguồn gốc từ khoáng sét tự nhiên đã được tổng hợp tại phòng thí nghiệm để phục vụ cho mục đích tổng hợp nhiên liệu sinh học. Nếu phản ứng được vận hành tại điều kiện tối ưu thì hiệu suất phản ứng chuyển đổi ester có thể đạt được từ 95 – 99 %.

Từ khóa: sản xuất nhiên liệu sinh học, triglyceride / dầu thực vật, xúc tác dị thể, FAMES.