

Biodiesel Production Using Metal Oxide Catalysts under Microwave Heating

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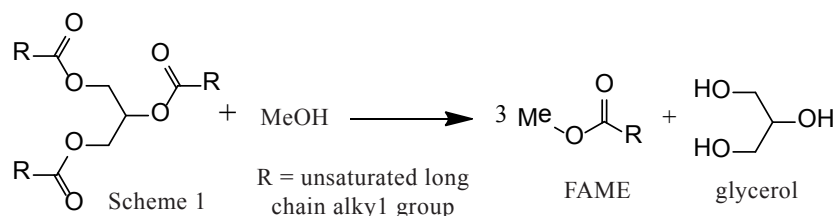
Abstract

Biodiesel has been commercially produced by transesterification of triglyceride with homogeneous base catalyst, where the separation of catalysts, glycerol and biodiesel from the product is troublesome. The solid catalyst can be used to resolve the separation problem and available to be reused. In this study metal oxide catalysts (PbO_2 , MnO_2 , Bi_2O_3 , Fe_3O_4 , TiO_2 , Fe_2O_3) were selected for the transesterification. Purity of fatty acid methyl ester (FAME) in the products, which is equivalent of FAME yield, was determined for these catalysts under pressurized microwave heating condition (200°C and 1.9 MPa). More than 89% of FAME purity was achieved with PbO_2 and MnO_2 catalyst for 30 minutes.

Keywords: microwave, biodiesel, high pressure, solid catalyst, metal oxide

1 Introduction

Biodiesel can be used as an alternative fuel without any engine modification and is a nontoxic, biodegradable fuel [1]. The most common method of biodiesel production is transesterification of triglyceride (Scheme 1) with methanol in the presence of homogeneous catalyst, producing a mixture of fatty acid methyl esters (FAME) and glycerol. Homogeneous acid catalysts require high methanol-oil ratio and long reaction time compared to homogeneous base catalysts, resulting the high production cost. Therefore, industrial process prefers base catalysts such as KOH and NaOH. The residual base catalyst dissolves almost in the glycerol phase and partially in the FAME phase, which makes the product separation difficult. As a result, a large amount of water is required to remove excess catalyst, increasing the production cost and causing the waste water issue.



reaction rate. The transesterification with heterogeneous catalyst is low reaction rate, requiring high temperature and pressure. Supercritical methanol transesterification can solve these problems by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state [7,8]. However, the reaction requires a temperature of 525-675 K and a pressure of 35 to 60 MPa. Supercritical methanol transesterification with CaO catalyst can slightly reduce the temperature to 520 K to obtain 90% conversion for the several minutes [9].

The principle advantage of microwave heating is based on the fact that heat is generated within the reacting substance itself, shortening the reaction time. The microwave-assisted transesterification with homogeneous catalyst has been reported by many researchers [10]. However, the usage of heterogeneous

The heterogeneous catalyst is environmentally benign, noncorrosive to the reactor, no soap forming with free fatty acid (FFA) and reusable. Transesterification reaction was catalyzed by the supported alkaline catalyst [2-4], alkaline earth oxides [5] and hydrotalcite [6]. In addition, the transesterification of triglyceride with methanol is a two-phase system which has a limited mass transfer rate between the reactants, thus slow down the overall

catalyst for the microwave-assisted transesterification was limited largely to MgO [11], CaO [11, 12], SrO [11,13] and BaO [11]. Transition metal oxide and the other metal oxides such as PbO_2 and Bi_2O_3 as a catalyst for the microwave-assisted transesterification was previously unreported to the best of our knowledge.

In this study, the transesterification of cooking oil with methanol in the presence of heterogeneous metal oxide catalysts (PbO_2 , MnO_2 , Bi_2O_3 , Fe_3O_4 , TiO_2 and Fe_2O_3) in a pressurized reactor under microwave irradiation was investigated. The reusability of MnO_2 catalyst with high reaction activity was examined.

2 Experimental

The metal oxide (PbO_2 , MnO , Bi_2O_3 , Fe_3O_4 , Fe_2O_3) and $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$ used as a catalyst were purchased from Kanto Chemical Co., INC., Japan and the TiO_2 catalyst was purchased from Wako Pure Chemical Industries Ltd., Japan. The transesterification reactions were carried out in a pressurized microwave reactor (Discover SP, CEM CO.), 2.85 mmol of cooking oil (molecular weight of triglyceride = 880), 5.0 mol% of the catalyst (based on ester group of cooking oil) and 0.63 g of methanol were charged into a closed pressure tube with a stirrer bar. The molar ratio of methanol to the oil was 6.9:1. The tube was attached to the pressurized microwave reactor. The mixture was irradiated by microwave (2.45 GHz, 300 W) for 30 min. The experiments were carried out at a pressure of about 1.9 MPa and a temperature of about 200°C. After microwave irradiation, the tube was set aside for one day to separate glycerol and FAME phase. The conventional heating experiments were performed with PbO_2 catalyst in the open reactor with a condenser at 80°C and ambient pressure.

After the separation, the catalyst was removed from the glycerol phase by filtration and the excess methanol was removed from FAME phase in vacuo. The purity of FAME and residual TG in the products were determined from the analysis of a high performance liquid chromatography in external standard method.

MnO_2 and PbO_2 catalysts were found to show the high reaction

activity under the pressurized microwave irradiation condition from the preliminary experiments. Regarding the toxicity of lead in PbO_2 catalyst, the reuse test of MnO_2 catalyst was performed considering for commercial use. The solid MnO_2 catalyst after the first run was washed with 10 mL of n-hexane for three times and dried in vacuo. The MnO_2 catalyst was employed for four successive cycle under the same experimental and regeneration methods.

3 Results and Discussion

3.1 Effects of reaction condition and metal oxide on FAME production

Table 1 shows the results of FAME production under microwave irradiation with high pressure in the presence of various metal oxide catalysts for 30 min. PbO_2 and MnO_2 indicated high catalytic activity for the transesterification of cooking oil under microwave heating. As a result of catalyst screening of metal oxides under conventional heating, the PbO_2 and MnO_2 catalysts indicated high catalytic activity at 215–225°C [14,15]. The purity of FAME in the product for PbO_2 and MnO_2 catalysts was 93.6 % at Entry 1 and 89.2 % at Entry 3, respectively. The catalytic activities for transesterification of the other metal oxides, such as Bi_2O_3 , Fe_2O_3 , Fe_3O_4 , and TiO_2 were extremely low. A solid $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$ catalyst was evaluated for the transesterification and indicated moderate catalytic activity with the FAME purity of 33.4%. However, it was soluble in methanol at high temperatures. PbO_2 and MnO_2 are used as electrochemical anode materials in lead-acid batteries and dry cells, respectively. In addition, these materials are well known as a catalyst for methanol oxidation. Therefore, high FAME purity for PbO_2 and MnO_2 catalysts might be improved by the electronic localization in methanol.

Table 1 Catalytic activities of various catalysts^a

Entry	Catalyst	Time/min	Temp/°C	Pressure/MPa	FAME ^b /%	TG ^c /%
1	PbO_2	30	209	1.89	93.6	0
2	MnO_2	30	191	1.87	35.7	43.2
3	MnO_2	30	230	2.49	89.2	1.2
4	MnO_2	60	230	2.41	93.0	0
5	Bi_2O_3	30	189	1.88	5.1	89.8
6	Fe_3O_4	30	190	1.86	1.2	98.8
7	TiO_2	30	185	1.88	0.5	99.5
8	Fe_2O_3	30	197	1.88	0.3	99.7
9	$\text{Ac}_2\text{Zn}^{\text{d}}$	30	199	1.88	33.4	43.6

^a These reactions were carried out by using cooking oil (2.85 mmol), metal oxide (5.0 mol%) and methanol (20.0 mmol). ^b Purity of FAME. ^c Purity of TG. ^d Ac_2Zn indicates $(\text{CH}_3\text{CO}_2)_2\text{Zn}\cdot 2\text{H}_2\text{O}$.

To verify the role of microwave irradiation, microwave and conventional heating experiments were performed with PbO_2 catalyst in the open reactor with a condenser at 80°C and ambient pressure. The purity of FAME was 1.0 and 7.2 % under the condition of conventional and microwave heating, respectively, as indicated in Table 2. The transesterification reaction at high temperature (209°C) in the pressurized reactor dramatically accelerated the reaction rate and also improved the miscibility between methanol and fatty oil. As a result, a high FAME purity was obtained in the pressurized reactor under microwave irradiation. However, PbO_2 cannot be used as a practical catalyst of FAME production because of its high toxicity. The activity of MnO_2 gradually increased with reaction temperature, pressure, and microwave irradiation time (Entries 3 and 4 in Table 1).

Naturally occurring MnO_2 usually contains impurities and a considerable amount of Mn (III) oxide. The missing positive charge has to be compensated by protons. Then OH^- ions would

be formed when the protons bound to the neighboring oxide ions and served as a transesterification catalyst.

3.2 Reuse tests of recovered MnO_2 for FAME production

Reuse tests of MnO_2 catalyst was carried out four cycle times (Entries 13-16 in Table 3). FAME purity of the first run for the fresh MnO_2 catalyst was 85.4% under the conditions of the cooking oil (2.50 g), methanol (0.65 g), and MnO_2 (24.7 mg) under pressurized microwave irradiation. The FAME purity of 85.4%, 76.3%, 77.6% and 73.7% was achieved after the first to fourth reaction cycle, respectively. The decline of FAME purity from the fresh and the reuse MnO_2 catalyst was obvious but the catalytic activities were almost maintained for the reuse catalyst. Activation procedures of the reuse catalyst is an issue in the future research. The results suggest that MnO_2 is a recyclable solid catalyst for FAME production.

Table 2 Effects of temperature, pressure and microwave irradiation on FAME production with PbO_2 catalyst^a

Entry	Heating method	Molar ratio of Methanol to oil	FAME ^b /%	TG ^c /%
10	Conventional heating at 80°C , 0.10 MPa	6.84	1.0	97.3
11	Microwave heating at 80°C , 0.10 MPa	6.90	7.2	83.1
12	Microwave heating at 209°C , 1.89 MPa	6.91	93.6	0

^a The reaction time was fixed at 30 minutes and the catalyst concentration was 5.0 mol%.

^b Purity of FAME. ^c Purity of TG.

Table 3 Reuse test of MnO_2 catalyst under pressurized microwave heating^a

Entry	Catalyst Cycles	Cooking Oil/g	Methanol/g	MnO_2 /g	FAME ^b /%	TG ^c /%
13	1	2.5	0.65	0.0247	85.4	0
14	2	1.9	0.48	0.0101	76.3	3.5
15	3	1.6	0.41	0.0089	77.6	4.0
16	4	1.2	0.30	0.0063	73.7	2.9

^a These reactions were carried out at 250°C and 2.0 MPa for 60 min. ^b Purity of FAME. ^c Purity of TG.

4 Conclusions

In FAME production from cooking oil, MnO_2 and PbO_2 had high catalytic activity for the transesterification under pressurized microwave irradiation. MnO_2 showed high activity due to the unique redox properties of solid MnO_2 at high temperature (230°C), high pressure (2.41-2.49 MPa), and long irradiation time (60 min). In addition, MnO_2 was demonstrated to be a recyclable solid catalyst for FAME production from cooking oil.

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