Transesterification of Soybean Oil Using KOH/KL Zeolite and Ca/Undaria pinnatifida Char

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Solid base catalysts for biodiesel production were synthesized by impregnating basic metal species on two support materials with large specific surface area: zeolite and pyrolysis char. KL zeolite and Undaria pinnatifida char were impregnated with KOH aqueous solution and calcium nitrate solution, respectively, to enhance the basic strength. The catalysts synthesized were characterized using Hammett indicators and CO₂-TPD analysis. Biodiesel was produced using soybean oil and methanol over the catalysts synthesized. The content of fatty acid methyl esters was measured to evaluate the catalytic activity. Generally, the catalytic activity increased with increasing quantity of basic metal impregnated but impregnation of excessive amount of metal could cause reduction in the activity.

Keywords: biodiesel, char, KL, basicity

1. Introduction

Biodiesel is composed of fatty acid alkyl esters obtained from transesterification of animal fat or vegetable oil. Owing to its similar physical and chemical properties to those of conventional diesel fuel, it can replace or be blended with diesel fuel. When blended with diesel fuel, biodiesel can reduce the emissions of CO₂, toxic pollutants, and particulate matter as well as improve the cetane number and lubricability[1]. Based on the life-cycle assessment of the biodiesel produced from soybean oil, Sheehan et al. reported that pure biodiesel (BD100), compared to petroleum diesel fuel, reduced the CO₂ emission by 78.54%, while the mixture of 20% of biodiesel with 80% of petroleum diesel (BD20) used for buses reduced the CO₂ emission by 15.66%[2].

In the transesterification reaction, triglyceride, the main components of fat and oil, reacts, in the presence of catalyst, with alcohol at the molar ratio of 1 : 3 to produce 3 moles of fatty acid ester and 1 mole of glycerol. Methanol is usually used due to its low price and small molecular mass. Base catalysts are used in commercial production of biodiesel to enhance the reaction rate. Homogeneous catalysts, such as KOH and NaOH are representative base catalysts used for the production of biodiesel. The homogeneous catalysts are widely used owing to several strengths including low price, high reaction rate, and relatively low reaction temperature and pressure. Nevertheless, homogeneous catalysts are dissolved in the reactant, disabling recovery and reuse of the catalysts, requiring neutralization and washing of the products, increasing the biodiesel production cost, and leaving large quantity of wastewater.
Heterogeneous catalysts can be recovered easily after the reaction, making the refining process simple. A main shortcoming of heterogeneous catalysts is the low transesterification reaction rate, compared to homogeneous catalysts, because the diffusion resistance obstructs the reaction in the oil-methanol-catalyst three-phase system[3]. Employment of a support with a large specific surface area can minimize the mass transfer limitation and enhance the reaction rate in liquid-phase heterogeneous-catalyst systems. Zeolite and char are representative support materials with a number of micropores on the surface and large specific surface area for impregnation of basic metals[8-10].

Zeolite is a microporous aluminosilicate mineral that is used as adsorbent or cracking catalyst in the petroleum chemical industry. Depending on its structure, zeolite has different pore shape and surface characteristics, resulting in different catalytic activity.

Positive ions as well as water molecules can enter the pores freely. Zeolite upgraded by ion exchange of basic positive ions or by impregnation of basic metal salts is used as base catalyst where base sites are required for active reaction. The basic strength of ion-exchanged zeolite increases with increasing electropositivity of the exchanged positive ions. Impregnation of basic metal salts can enhance the basicity by producing basic metal oxide clusters inside the zeolite structure[4].

The structure of L zeolite used in this study was invented by Barrer and Villiger. L zeolite has one-dimensional channel-type pores. The 0.71 nm pore opening is connected to a cavity with a dimension of 0.48 × 1.24 × 1.07 nm. Owing to its characteristic structure, it is used commercially for aromatization of C6 hydrocarbons and for the Chevron Aromax catalytic process[5].

Pyrolysis is a process in which organic materials are decomposed under an oxygen-free condition into char, oil, and gas by externally provided heat. Pyrolysis of biomass for the purpose of producing oil and gas as energy sources is under extensive investigations. In particular, marine algae are advantageous over other biomass in terms of the rate of growth and usable cultivation area. Pyrolysis of marine biomass produces a carbon structure with a very large specific surface area similar to activated carbon, called char, resulting from the formation of micropores during the decomposition of cell wall.

In this study, KL zeolite and pyrolysis char derived from Undaria pinnatifida were employed as catalyst support. Basic metal salts were impregnated on these support materials to enhance the basicity. The catalysts synthesized in this way were used as solid catalysts for the production of biodiesel.

The Si/Al ratio of the L zeolite used in this study is 6.1. It was impregnated with KOH aqueous solution to increase the basicity. Biodiesel was generated using different amounts of catalyst to examine the activity of the catalyst. Char was impregnated with calcium nitrate using the excess wetness impregnation method to increase the strength and quantity of base sites. The fatty acid methyl esters (FAME) content was measured to evaluate the quality of the biodiesel produced.

2. Experimental

2.1. Synthesis of Catalysts

The basic strength of KL Zeolite (TOSOH, Si/Al = 6.1) was enhanced by impregnating it with KOH. 5, 10, 20, and 30 wt% of KOH, relative to zeolite mass, was dissolved in 15 mL of distilled water. This solution was added to the zeolite slowly for impregnation. The impregnated catalyst was dried for 24 h in a 110 °C oven. It was then ground finely before calcination for 4 h in a 500 °C furnace.

The char was produced as a byproduct from the pyrolysis of Undaria pinnatifida in a fluidized-bed reactor. Initial feed size was 1∼1.7 mm, with the feeding rate of 3∼4 g/min. Pyrolysis was conducted at 500 °C under a nitrogen atmosphere. It was impregnated with calcium nitrate using the excess wetness impregnation method to enhance the basic strength. Calcium nitrate aqueous solution with the calcium amount of 3, 5, and 10 wt%, relative to the char mass, was added to the char for impregnation. The impregnated char was dried for 24 h in a 110 °C oven. It was then calcined for 1 h at 500 °C under an oxygen-free condition.

2.2. Production and Analysis of Biodiesel

Soybean oil was used as the reactant oil. Soybean oil is most widely used for the production of biodiesel in Korea because of its low price and large supply. Methanol (Duksan, 99.8%) was used for the transesterification reaction. GC-grade reagents were used for the analyses.

An atmospheric-pressure 4-neck double-jacket batch reactor with 1000 mL volume was used. Water bath circulator was used to control the reactor temperature. A reflux condenser was installed to prevent evaporation of methanol. A stirrer equipped with a Teflon impeller was installed.

Although the stoichiometric molar ratio of oil and alcohol for transesterification reaction is 1 : 3, excess alcohol is usually used to obtain high reaction rate. In this study, the oil-methanol ratio of 1 : 12 was used. To prevent the loss of methanol during the reaction, reactor temperature was maintained at 333 K, which is lower than the boiling point of methanol. Catalyst was introduced and stirring was started when the temperature of methanol and oil reached the set temperature, which was regarded as the reaction initiation. After the reaction was completed, catalyst powders were removed by filtration. The product was separated clearly into 2 phases : yellow biodiesel phase (upper phase) and brown glycerin phase (lower phase). The upper phase was taken and remaining methanol in it was evaporated in a rotary evaporator before measuring its FAME content.

The FAME content is an important quality standard for commercial biodiesel. In the case of BD100, the FAME content must be 96.5% or higher. The FAME content of the biodiesel produced in this study was measured by GC-FID equipped with an HP-INNOWA column (30 m × 0.320 mm × 0.25 µm). The FAME wt% was calculated using the following formula:

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\text{FAME wt\%} = \frac{\text{FAME area}}{\text{Total area}} \times 100
\]
$$C = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100$$

where
\(\sum A\) : total peak area of methyl esters from C14 to C24 : 1
\(A_{EI}\) : peak area corresponding to methyl heptadecanoate
\(C_{EI}\) : concentration of methyl heptadecanoate solution used (mg/mL)
\(V_{EI}\) : volume of methyl heptadecanoate solution used (mL)

3. Results and Discussion

3.1. KOH-KL Zeolite Catalyst

The specific surface area of KL zeolite before the impregnation of KOH was 280 m$^2$/g. After the impregnation, it was impossible to measure the specific surface area. Because the KOH-impregnation made the zeolite crystallized, it had to be ground finely with a mortar. During the grinding, pores were possibly blocked, preventing the nitrogen adsorption. The basic strength was measured using the Hammett indicator method, in which the basic strength is determined by the color change of acidic indicator adsorbed on solid surface. Methanol and Hammett indicators were mixed with 50 mg of catalyst sample and the mixture was stirred until sufficient color change was observed[6,7].

Non-impregnated KL zeolite was color-developed by bromothymol blue indicator but not by phenolphthaleine indicator, indicating that its basic strength is H$_\text{pK}_a$ = 7.2–9.6. On the other hand, the KOH-impregnated KL zeolite was color-developed by phenolphthaleine indicator but not by 2,4-dinitroaniline indicator, indicating that its basic strength is H$_\text{pK}_a$ = 9.6–15.0. Measurement of basic strength using benzoic acid indicator was not possible because adsorbed KOH was dissolved in methanol, resulting in overestimation of the basicity.

The acid value of the soybean used in the experiment was measured to be 0.8 mg-KOH/g, excluding the requirement of pre-treatment with acid catalyst. The quantity of catalyst used for transesterification reaction was 4, 7, and 10 wt%, relative to the oil mass.

Figure 1 and Table 1 show the FAME content of the biodiesel produced under different conditions. The catalyst that was not impregnated with KOH did not produce FAME at all. Although there are base sites present inside the pores, they did not seemingly promote the reaction probably because the pores are too small. The FAME content in biodiesel increased with increasing quantity of KOH impregnated and with increasing catalyst dose.

The KL zeolites impregnated with 20% and 30% KOH, which showed good performance, were recovered by filtration and reused once. 7 wt% of catalyst relative to the oil mass was used. Table 2 compares the results obtained using the fresh and recovered catalysts. The FAME contents obtained using the recovered catalysts were significantly lower than those obtained using fresh catalysts, probably because KOH impregnated on the zeolite surface was dissolved in methanol in the first experiment, reducing the basicity.

3.2. Undaria pinnatifida Char Catalyst

Ca content is considered an important factor determining the activity of a solid base catalyst. Table 3 lists the contents of metal components contained in the char catalysts impregnated with different amounts of Ca. ICP-AES was used for the measurement of metal contents. The pristine char before impregnation was shown to contain significant quantity of Ca. The Ca content increased with increasing Ca loading. CO$_2$-TPD was used to measure the strength and quantity of base sites present on the catalyst surface more accurately (Figure 2). The catalysts
with 3% and 5% Ca loading showed the peak at a higher temperature (127 °C), indicating that their basic strengths were higher, than that with 10% Ca loading.

10 wt% of char catalyst, relative to the oil mass, was used for each experiment. Table 4 lists the FAME contents of the biodiesel obtained with different Ca loadings. The Ca present in the pristine char before impregnation produced no FAME. The FAME content increased with increasing Ca loading up to 5 wt%. Increased basicity by Ca loading is believed to be the reason for the enhanced reaction activity. When 10 wt% of Ca was impregnated, however, the FAME content was lower than that obtained with 5% Ca loading because of the reduced basicity shown in the CO$_2$-TPD result (Figure 2).

4. Conclusions

The potentials of KL zeolite and Undaria pinnatifida pyrolysis char as the solid base catalysts for biodiesel production were evaluated.

KL zeolite was impregnated with KOH aqueous solution to enhance its basic strength. The FAME content of the biodiesel produced increased with increasing quantity of KOH impregnated. Reuse of the catalyst resulted in significant reduction of the catalytic activity because of the dissolution of KOH in methanol.

Undaria pinnatifida pyrolysis char was impregnated with calcium nitrate using the excess wetness impregnation method, to be used as a solid base catalyst. The catalytic activity of the char was the highest when 5% Ca was impregnated, while non-impregnated char showed no activity. Excessive impregnation with 10% Ca resulted in a reduction of the catalytic activity.

References