본 연구에서는 기존 MgO의 염기세기를 증가시켜 전이에스테르화 반응에 있어 보다 좋은 활성을 가지는 촉매를 만들고자 하였다. MgO를 실험실에서 제조한 후 지지체로 사용하였으며 염기세기를 증가시키기 위하여 KF를 함침법으로 담지하였다. BET, XRD, XRF, CO\textsubscript{2} TPO로 촉매의 특성분석을 하였고, 대두유와 메탄올을 사용하여 바이오디젤을 합성한 후 지방산메틸에스테르 함유량을 측정함으로써 촉매의 활성을 알아보았다. 결과적으로, KF를 30% 담지한 촉매가 활성이 가장 좋은 것으로 나타났다. 이는 전이에스테르화 반응에서 중간세기 염기도가 더 많이 관여하기 때문으로 보인다.

The basic strength of the MgO catalyst was enhanced by impregnating it with KF to synthesize a highly active catalyst for the bio-diesel production. To increase basicity, KF impregnated on synthesized MgO in laboratory. The synthesized catalyst was characterized using N\textsubscript{2} adsorption-desorption, X-Ray diffraction, X-Ray fluorescence, and CO\textsubscript{2} temperature programmed desorption analyses. Bio-diesel was produced from soybean and methanol and its fatty acid methyl ester content was measured to evaluate the activity of the catalyst. The catalyst impregnated with 30 wt% KF exhibited the highest activity, which was attributed to its abundant intermediate base site.

**Keywords:** biodiesel, transesterification, KF/MgO, basicity

1. Introduction

Imminent exhaust of fossil fuels and global warming derived lots of efforts to develop alternative energy technologies. Among others, bio-diesel is one of the most promising renewable energy sources. Bio-diesel is a mixture of fatty acid alkyl esters obtained through transesterification reaction of animal fats or vegetable oils. As its properties are similar to those of conventional diesel fuel, bio-diesel can be used as a pure fuel or blended with petroleum diesel to be used in diesel engines.

Bio-diesel is biodegradable, needs no alteration of engines, and emits less air pollutants such as sulfur dioxide than conventional diesel[1]. Based on a life-cycle assessment of bio-diesel produced from soybean oil, Huo et al.[2] reported that the greenhouse gas emission can be reduced considerably compared to fossil fuels. In certain conditions, application of clean development mechanism is also possible.

† 교신저자 (e-mail: catalica@uos.ac.kr)

In the transesterification reaction, one mole of triglyceride contained in animal fats or vegetable oils react with three moles of alcohols under the presence of catalysts to produce three moles of fatty acid alkyl esters and one mole of glycerols. Methanol is usually used as the alcohol because it is cheap and its molecular mass is small. Because the transesterification reaction is a reversible reaction, alcohol is provided in excess to obtain a high yield, while acid or base catalysts are used to promote the reaction rate.

Homogeneous catalysts such as KOH and NaOH are representative base catalysts used for the transesterification reaction. These catalysts have been widely used because of their low price, high reaction rate, and high reactivity at mild condition, e.g., under low temperature and pressure. These homogeneous catalysts, however, are dissolved in alcohol making their recovery and reuse difficult and requiring neutralization and washing of the products. This leads to an increase of production cost of bio-diesel and generation of a large amount of waste water imposing an adverse impact on the environment. Therefore, investigation on the use of heterogeneous catalysts for bio-diesel pro-
duction, which enables recovery and reuse of the catalysts and simplifies the purification process, has been extensively carried out. Generally, base catalysts exhibit better activities than acid catalysts although pretreatment using acid catalysts may be required when the content of free fatty acids is high. Various solid base catalysts, including zeolite, alkaline-earth metal oxides, and hydrotalcite, have been applied to bio-diesel production[3,4].

Of the alkaline-earth metal oxides, magnesium oxide (MgO) has been used as the solid base catalyst by a number of researchers[5-7]. According to these studies, MgO showed low activity for the transesterification reaction of vegetable oil, requiring the reaction to be carried out for long time or at a high temperature[5]. Therefore, efforts have recently been made to increase its basic strength through various treatments.

In this study, KF impregnation to increase the basic strength of MgO was examined to develop a catalyst that has a high activity for the transesterification reaction. MgO having a high surface area was synthesized at the laboratory to be used as the catalyst support[8]. It was then impregnated with KF to increase its basic strength[8]. N$_2$ adsorption-desorption, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), and CO$_2$ temperature programmed desorption (TPD) analyses were used to characterize the catalyst synthesized in this way. Bio-diesel was produced from soybean oil and methanol over the synthesized catalyst. The content of fatty acid methyl ester (FAME) was measured to examine the activity of the catalyst.

2. Experimental

2.1. Synthesis of the Catalyst

As the surface area of commercial MgO is too small, MgO having a high surface area had to be synthesized in this study to be used as the support. Two moles of magnesium nitrate (Mg(NO$_3$)$_2$·6H$_2$O) (512.82 g) were dissolved in 1000 mL of distilled water. Two moles of sodium carbonate (Na$_2$CO$_3$) (211.98 g) and two moles of sodium hydroxide (NaOH) (80 g) were dissolved together in 2000 mL of distilled water to prepare a precipitation solution. Both the magnesium nitrate solution and the precipitation solution were heated to 80 °C for 2 h, washed three times with distilled water, and then added drop by drop to 20 mL of distilled water, while maintaining pH at 10 and stirring the solution to allow effective reaction and precipitation of MgO to take place. The precipitation was put in an oven set at 100 °C for 24 h, washed three times with distilled water, and dried in the oven again for 24 h. The dried MgO precipitation was then pulverized into 60–200 mesh size and calcined for 3 h at 500 °C. The excess water method was used to synthesize KF/MgO catalyst used in this study. Three different amounts of KF, 2, 4, and 6 g, were dissolved into 100 mL of distilled water. After inserting 20 g of MgO into the KF solution, the solution was heated weakly for 2 h in a vacuumed rotary evaporator to evaporate moisture completely. The catalyst synthesized in this way was dried in the oven for 12 h at 100 °C and then pulverized into 60–200 mesh size.
reaction rate. In this study, a molar ratio of 1 : 12 was used. To minimize the loss of methanol, the reactor temperature was controlled at 60 °C, which is lower than the boiling point of methanol. When the temperature of methanol and oil reached the set temperature, catalyst was inserted and stirring was began, which was regarded as the starting time of the reaction. After completion of the reaction, catalyst was removed by filtration. The product was clearly divided into two phases: a brown glycerol phase (lower phase) and a yellow bio-diesel phase (upper phase). After recovering the upper phase, residual methanol was removed in a rotary evaporator and the FAME content was analyzed.

The FAME content of bio-diesel is an important quality standard and it has to be equal to or higher than 96.5% for commercial BD100. GC-FID equipped with a 30 m × 0.320 mm × 0.25 µm HP-INNOWA column was used to analyze the FAME content. The FAME wt% was calculated based on the following equation:

\[ C = \frac{(\Sigma A) - A_{EL}}{A_{EL}} \times C_{EL} \times V_{EL} \times 100 \]

\( \Sigma A \) : total peak area of methyl esters from C14 to C24 : 1
\( A_{EL} \) : peak area corresponding to methyl heptadecanoate
\( C_{EL} \) : concentration of methyl heptadecanoate solution used (mg/mL)
\( V_{EL} \) : volume of methyl heptadecanoate solution used (mL)
\( m \) : mass of sample (mg)

3. Results and Discussion

3.1. Characteristics of the Catalyst

The BET surface area of the KF/MgO catalyst synthesized in this study is shown in Table 1. The surface area of pure MgO before impregnation was 29 m²/g. When it was impregnated with 10, 20, and 30 wt% KF without calcination, the surface area was shown to be 23, 21, and 8 m²/g, respectively; the BET surface area decreased with increasing amount of KF impregnated. In particular, the BET surface area decreased dramatically from 21 to 8 m²/g when the amount of KF was increased from 20 to 30 wt%.

The effect of the amount of KF impregnated on KF/MgO catalyst on the XRD pattern is shown in Figure 2. It is shown that Mg(OH)₂ peaks are dominant, while very weak MgO peaks are also observed. This result indicates that most MgO was converted into Mg(OH)₂ during the KF impregnation process of MgO support.

The characteristic peak of KF (33.6) was not observed from the XRD pattern of the KF/MgO catalyst synthesized in this study. This result implies that KF was dispersed very well preventing formation of large clusters, which is in accordance with the results of previous studies[6,7]. According to Wan et al.[6], fluoride ions (F⁻) that are not coordinated enough in KF-containing base catalysts play a role as active sites. They also reported that these active sites are lost at 973 K or higher. As KF was dispersed well in the KF/MgO catalyst synthesized in this study, it was expected that there were sufficient fluoride ions which could act as the active sites.

3.2. Basicity of the Catalyst

\( \text{CO}_2 \)-TPD is frequently used to measure the amount and the strength of base sites[8-10]. According to \( \text{CO}_2 \)-TPD results of the KF/MgO catalyst. Pure MgO showed the maximum peak at 136 °C, which represents weak base sites of bulk MgO. When KF was impregnated, the peak temperature of the weak base sites was a little higher (143 °C) than that of pure MgO. In addition, base sites with intermediate strength appeared over the temperature range of 200
Table 2. The Effect of the Loading Ratio on the Reaction

<table>
<thead>
<tr>
<th>Catalyst (KF loading wt%)</th>
<th>FAME wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF/MgO (10%)</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>KF/MgO (20%)</td>
<td>36.60</td>
</tr>
<tr>
<td>KF/MgO (30%)</td>
<td>92.91</td>
</tr>
</tbody>
</table>

∼350 °C for the KF/MgO catalyst, which was not the case for pure MgO. The peak temperature of these intermediate-strength base sites increased from 215 °C (through 270 °C) to 320 °C, i.e., the basic strength increased, when the amount of KF impregnated was increased from 10 wt% (through 20 wt%) to 30 wt%.

When the areas of the TPD curves shown in Figure 3 that denote the amounts of the base sites are compared, the 10 wt% KF-impregnated catalyst showed the highest area, while the area decreased with increasing amount of KF impregnated although it is still higher than that of pure MgO, which is in agreement with our previous study[9]. This result indicates that impregnation of MgO with small amount of KF increases the amount of base sites but impregnation with excess amount of KF leads to covering of active sites on the catalyst surface and hence reduction of surface area, which more than compensates for the increase of base sites.

3.3. FAME Analysis of Bio-diesel

Table 2 shows the FAME contents of the bio-diesels produced with different KF loadings in this study. The FAME content increased with the KF loading. When the KF loading was 10% or lower, little activity was observed. This relationship between the FAME content in product bio-diesel and KF loading is in accordance with previous studies[6,11].

Although the catalyst impregnated with 10% KF had the largest amount of base sites as shown in the TPD analysis result, their basic strength was weak, resulting in weak activity. On the other hand, the catalyst impregnated with 30% KF, which had strongest base sites, exhibited the highest activity in spite of its small number of base sites. This result indicates that the effect of basic strength is more important than that of the amount of base sites for the quality of bio-diesel produced.

4. Conclusions

MgO catalyst impregnated with KF to enhance the basic strength was used for the transesterification reaction. While the TPD analysis showed that the catalyst impregnated with 10 wt% KF had the largest amount of base sites, the catalyst with 30 wt% KF showed the highest catalytic activity for the transesterification reaction. This result indicates that the strength of the intermediate base sites is a more important factor for the transesterification reaction than the amount of the base sites.

References